

A Derivation and Analysis of Phase Field Models of Thermal Alloys

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We derive a system of equations describing a binary mixture with thermal properties and a phase transition. The system involves the concentration, c , the temperature, T , and phase or order parameter, φ , and is the generalization of the phase field model for a pure material. Transition layers of width ε are exhibited by φ , c , and $\nabla T \cdot \hat{n}$. In the limit as ε approaches zero, with all other physical parameters held fixed, one attains a limiting set of sharp interface equations which generalize the traditional small ε systems of equations. The derivation is accomplished by a systematic use of thermodynamic principles and includes as a special case the phase field equations for a pure material. The phase diagram is recovered in equilibrium. © 1995 Academic Press, Inc.

1. INTRODUCTION

The study of the dynamics of phase boundaries can be grouped into two general categories: (a) models which involve a mathematically sharp interface with explicit conditions imposed; (b) a diffused interface approach in which the interface is defined, for example, as the set of points where an *order parameter* φ takes on a specified intermediate value (e.g., if $\varphi = 0, 1$ in the pure phases, then $\varphi = \frac{1}{2}$ may define the interface). In the mid-1980s, a close relationship was established between these two types of models [1–2].

For a pure material in a region $\Omega \subset \mathbb{R}^d$, a reasonable sharp interface problem can be written in terms of the temperature, T , and interface, $\Gamma(t)$, as

$$C_v T_t = k \Delta T \quad \text{in } \Omega \setminus \Gamma(t), \quad (1.1)$$

$$lv = -k[\nabla T \cdot \hat{n}]_{\pm}^+ \quad \text{on } \Gamma(t), \quad (1.2)$$

$$T - T_M = -\frac{\sigma}{[s]_{\text{eq}}} (\kappa + \alpha v) \quad \text{on } \Gamma(t). \quad (1.3)$$

Here, C_v is the specific heat per unit volume, k is the thermal conductivity, l is the latent heat per unit volume, σ is the surface tension, α is the relaxation scaling, s is the entropy per unit volume, and $[\cdot]_{\text{eq}}$ is the equilibrium difference between liquid and solid, while $[\cdot]_{\pm}^+$ is the jump in the quantity as one crosses the interface from solid to liquid. The (normal) velocity to the interface $\Gamma(t)$ at (x, t) is denoted

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$v(x, t)$ or v , and the sum of principal curvatures at (x, t) on $\Gamma(t)$ is denoted $\kappa(x, t)$ or κ . Subject to suitable initial and boundary conditions, which depend on the particular physical application, the problem can be stated as finding $T(x, t)$ and $\Gamma(t)$ which satisfy the surface tension and kinetics model, (1.1)–(1.3).

The oldest of these models, known as the classical Stefan model, is the special case which is obtained by setting $\sigma = 0$ in (1.3), so that $T - T_M = 0$. The difference between the two models ($\sigma \neq 0$ and $\sigma = 0$) is quite profound from both a physical and a mathematical perspective. Setting $\sigma = 0$ eliminates an important physical length scale, namely the capillary length, $d_0 := \sigma/[s]_{\text{eq}}$, which is crucial in the selection of the velocity of single-needle dendrites [3–5] and the stability properties of the interface [6–7]. The absence of any length scale in the problem, together with dimensional analysis, implies that the velocity can be determined at most as a multiple of curvature. The mathematical issues are equally serious since the sign of $T(x, t)$ determines the phase if $\sigma = 0$, so that $T(x, t) > 0$ defines the liquid state and $T(x, t) = 0$ is by definition the boundary between liquid and solid ($T < 0$). When $\sigma \neq 0$, the sign of the temperature no longer determines the phase, so that the dual role of T in determining both temperature and phase becomes particularly awkward in light of (1.3). Hence, the mathematical formulation based on the single variable T is considerably less elegant when $\sigma \neq 0$, particularly since the description clearly fails when the interface intersects with itself or exhibits other singularities preventing the existence of the classical curvature or normal to the interface. Thus, the curvature must then be considered in some weak sense, the precise choice of which determines the interface behavior. Moreover, if this weak sense of curvature is not derived from physics, then it is unlikely that the interface will exhibit the correct motion upon the commencement of self intersections or singularities. Consequently, even the study of the sharp interface problem leads naturally to an order parameter approach.

An alternative formulation of phase boundary problems along the lines of (b) is the phase field model in which an order parameter, $\psi(x, t) = 2\varphi(x, t) - 1$, is employed. In the distinguished limit of the surface tension and kinetics model (i.e., as interface thickness approaches zero, while σ and α remain fixed at non-zero values) one can write the system of differential equations for (T, ψ) as

$$C_r T_t + \frac{l}{2} \psi_t = k \Delta T \tag{1.4}$$

$$\alpha \varepsilon^2 \psi_t = \varepsilon^2 \Delta \psi + \frac{1}{2} (\psi - \psi^3) + \varepsilon \frac{[s]_{\text{eq}}}{3\sigma} (T - T_M), \tag{1.5}$$

where ε represents the thickness of the interfacial layer and all other parameters are the same as previously defined. The interface is now defined as the set of points, where ψ vanishes. Equation (1.5) arises from a free energy of the form

$$\mathcal{F}\{T, \psi\} = \int d\mathbf{x} \left\{ \frac{1}{2} \xi^2 (\nabla \psi)^2 + \frac{1}{8a} (\psi^2 - 1)^2 - 2T\psi \right\}, \tag{1.6}$$

where ξ is a length scale and a measure of the microscopic bonding and a is a measure of the depth of the double-well $(\psi^2 - 1)^2$. In terms of macroscopic properties, $\varepsilon := \xi a^{1/2}$ is the interface thickness (see Section 6 or [1], [2]) and $\sigma := \frac{2}{3} \xi a^{-1/2}$ is the interface tension [8].

The time evolution is governed by the kinetic equation $\psi_t = -A \delta f / \delta \psi$, where f is the integrand of (1.6), so that ψ is restored to equilibrium with a “force” which is proportional to the extent to which it is out of equilibrium. Coupling this equation with a simple energy balance equation (1.4) completes the model. The derivation we present in Sections 2–5 for a mixture will include this pure model as a special case.

The approach has its origins in Landau theory [9], Cahn–Hilliard type equations [10, 11], and the application of mean field theory to critical phenomena [12]. Phase field theories are generally rooted in the idea that each atom, or “spin,” behaves in reaction to an average “field” created by all other spins. This, of course, is a vast simplification over evaluating the sum over all possible states to calculate the partition function and, thereby, the free energy. Thus, the variable $\psi(x, t)$ represents the mean field description of the phase at each point (x, t) in space-time. This approach has been used with moderate success in the subtle area of critical phenomena, suggesting that this averaging process does not destroy the crucial aspects of cooperative phenomena. The usual theoretical justification for the use of an order parameter in critical phenomena involves the fact that the correlation length is very large. However, the use of these ideas in critical phenomena does not guarantee a priori that they can provide a successful description of ordinary phase transitions where the correlation length is typically a few angstroms [13]. Another difference between the critical region and ordinary phase transitions is that the study of critical phenomena can rely on universality, since the critical exponents do not depend on the quantitative details of the system. Hence, the requirement of quantitative answers in the absence of universality, together with the small correlation length necessitates an independent justification and subsequent examination of the results of phase field theories in the noncritical region.

Furthermore, in a system of dynamical nonlinear differential equations, such as the phase field, the bifurcation diagram can be expected to vary between completely different behaviors as the parameters vary. Consequently, the identification of specific parameters is crucial to even a qualitative understanding.

Various derivations of the phase field equations have been discussed in recent years [14–20]. A number of theoretical and computational results have demonstrated agreement with known experimental and theoretical results. For example, the existence of single-needle dendrites with constant velocity which is independent of initial conditions has been shown in computations of these equations [21]. More recently, similar studies have established key dendritic relationships [22–24]. Qualitative numerical studies with phase field equations are presented in [25–27]. Other applications of phase field methods include superconductivity [28–29] and chemical reactions [30].

The theoretical link between the phase field model (1.4), (1.5) and sharp interface models such as (1.1)–(1.3) has been established using formal matched asymptotic

analysis [1–2] (see also [31] for an alternate scaling) and also rigorous analysis [32–35] under various conditions. Specifically, in the limit $\varepsilon \rightarrow 0$, the solutions to (1.4), (1.5) are governed to leading order by those of (1.1)–(1.3). Other free boundary problems such as the classical Stefan model, the Hele–Shaw model, motion by mean curvature can all be derived in appropriate distinguished limits. While many of the theoretical results concern the limit $\varepsilon \rightarrow 0$, an important practical question for computations involves stretching ε beyond its true physical value of angstroms up to at least one mesh spacing in a reasonable computational grid. The computations [36] have shown that the phase field equations are close to the appropriate sharp interface problem even when ε is not small. Two preliminary reports on one form of the phase field equations which do not converge to any complete sharp interface model were written by Fix [37] and Caginalp [38], the latter of which was submitted in 1983 with further mathematical analysis in [8].

The computational advantages of the phase field system of equations include the following. (A) A broad range of phenomena, ranging from stable crystal growth to dendritic growth to motion by mean curvature, can all be computed with these equations with a single change of parameters. (B) The system has smooth solutions and does not involve conditions on the interface so that interface tracking is not necessary. (C) All of the physical parameters are clearly identified so that the equations can be used to obtain quantitatively reliable numbers. (D) Computations involving self-intersections of the interface do not pose difficulties for the phase field model.

A simple example illustrates this last advantage of the phase field approach as well as the additional analysis needed for a sharp interface model such as (1.1)–(1.3). Consider two solid spheres with a small space between them surrounded by their melt which is slightly undercooled so that the spheres grow slowly. Clearly, when the spheres touch, the curvature and normal velocity are no longer defined as classical quantities. Thus, (1.1)–(1.3) is not a sufficient description in this complex situation since (1.3) is a macroscopic approximation for simple geometries. Hence, the sharp equations (1.1)–(1.3) must be supplemented by another set of conditions describing the evolution under circumstances in which the classical normal and curvature are not defined. On the other hand, the phase field equations are guaranteed to have a smooth solution (ψ, T) if the initial and external boundary conditions are sufficiently smooth. The phase field equations naturally describe the evolution of intersecting interfaces, such as this example [22], since they are based on free energy considerations rather than a macroscopic derivation for a particular (smooth) geometry. Nevertheless, it is, of course, possible that a more accurate description of complex geometries could involve new dynamics which are nonlinear.

The theoretical and computational advantages of the phase field approach motivate the derivation and study of the analogous system of equations for binary mixtures or alloys, where similar difficulties and subtleties arise. Although the concentration and temperature together determine the phase of the material in equilibrium, one cannot use the concentration as the order parameter since the phase transitions we consider (e.g., liquid–solid) involve a process which cannot be

described by concentration alone, unlike some other transitions (e.g., order-disorder) in which concentration is the only issue. In equilibrium, knowledge of the temperature and concentration allows one to determine, via the lever rule, the fractions of total material in liquid and solid, but the use of the order parameter is necessary for more detailed information such as the phase at a particular point, which will depend on the geometry in equilibrium and the dynamics in non-equilibrium situations. Furthermore, in the type of phase transition we consider, the order parameter for the system is generally not conserved, while the concentration must be locally conserved.

In discussions at NIST in 1989 [39] a consensus arose that the correct approach to generalizing the phase field equations should involve a nonconserved order parameter coupled with a diffusion equation for concentration. This approach has been implemented in the isothermal ideal case [40, 41] to study a number of properties including solute trapping. In this paper we present a derivation and analysis of a set of equations for phase boundaries in a binary alloy (ideal or non-ideal) with thermal properties. In a companion paper [42], these equations and simplifications are studied asymptotically and are shown to reduce to the traditional sharp interface models in the limit as the interface thickness vanishes and as progressively more physics is removed from the equations.

Upon deriving the system of equations, we demonstrate that the limit as interface width vanishes ($\varepsilon \rightarrow 0$) leads to a system of equations with new interface conditions. The new interface conditions provide a description of the phase diagram so that the connection between the free energy and the liquidus and solidus lines of the phase diagram is established.

2. OVERVIEW OF DERIVATION

Throughout the derivation let subscripts denote the material ($i=1$ and $i=2$ for the first and second materials, respectively) and let superscripts denote the phase ($j=0$ for solid and $j=1$ for liquid). We use capital letters for extensive (i.e., total) thermodynamic quantities and lower case for intensive quantities. Thus G_i^j , S_i^j , U_i^j , V are the total Gibbs free energy, entropy, internal energy, and total volume of material i in equilibrium in phase j , and if n is the total number of moles of the material, then $g_i^j = G_i^j/n$, $s_i^j = S_i^j/n$, $u_i^j = U_i^j/n$, and the specific volume $v = V/n$ are the corresponding molar specific densities. A standard form for the total Gibbs free energy of a mixture composed of two materials in pure phase j is

$$G_{\text{mix}}^j = n_1 g_1^j + n_2 g_2^j + G_M + G_E, \quad (2.1)$$

where the *ideal free energy of mixing* G_M and the *excess free energy* G_E account for nonlinear concentration effects due to the mixing and are described in the following section. The corresponding intensive variables may not depend in an arbitrary way

on the extensive quantities n_i , n , but are functions of the local concentrations $c_i = n_i/n$ (this fact is a constraint on the form of G_M , G_E). The *binary phase diagram* for the mixture is defined by the pair of *phase equilibrium conditions*,

$$\mu_i^0 = \mu_i^1, \quad i = 1, 2, \quad (2.2)$$

where μ_i^j is the *chemical potential* of component i in phase j , defined by

$$\mu_i^j = \left(\frac{\partial G_{\text{mix}}^j}{\partial n_i} \right)_{P, T, n_{k \neq i}}. \quad (2.3)$$

We will assume throughout that the two materials have the same fixed specific volume, independent of temperature and phase, so that mechanical effects may be neglected (see [16] for a treatment of phase field equations with material flow). We will also assume that the *specific heat capacity*,

$$C_v = T \frac{\partial s_i^j}{\partial T} = -T \frac{\partial^2 g_i^j}{\partial T^2}, \quad (2.4)$$

is a constant independent of temperature and is the same for both materials. The methods are easily generalized to the case of distinct and temperature dependent specific heat capacities for the two materials. Integrating (2.4) in T gives

$$g_i^j = -C_v T \ln T + \xi_i^j T + \zeta_i^j \quad (2.5)$$

as the general form of the free energy density for the single phase pure material. The eight constants ξ_i^j , ζ_i^j may be related to the properties (entropies, internal energies, and melting temperatures) of the pure materials in phase equilibrium by evaluating the free energy densities (2.5), together with the equilibrium conditions (2.2) at the two melting temperatures $T = T_i$. Upon specifying the mixing and excess free energies G_I , G_E , in (2.1), and dividing by the number of moles n , the free energy densities g_{mix}^j of the mixture in the pure phases are completely determined.

The free energy densities for the mixture were constructed by adding the non-linear interaction terms G_I , G_E to the linear transitional term $n_1 g_1^j + n_2 g_2^j$. The Landau–Ginzburg free energy density for a two phase mixture may now be constructed in an analogous manner, by adding *phase interaction* terms to a linear transitional term of the form

$$g_0 = \phi g_{\text{mix}}^0 + (1 - \phi) g_{\text{mix}}^1. \quad (2.6)$$

We assume that the only interaction effects that need to be considered are the Landau potential and phase diffusion, so that the free energy density becomes

$$g = \frac{B(c)}{2} T |\nabla \phi|^2 + \frac{\alpha(c)}{4} T \phi^2 (1 - \phi^2) + g_0. \quad (2.7)$$

Once the free energy is known, the dynamical equations for c , T , and ϕ follow from general thermodynamic principles. The dynamical equation for ϕ ,

$$\frac{\partial \phi}{\partial t} = -A \frac{\delta g}{\delta \phi}, \quad (2.8)$$

is again determined by relaxation dynamics around equilibrium, where the time rate of change of ϕ is proportional to the variational derivative of the free energy, which vanishes in equilibrium. The diffusion equation (essentially conservation of mass) is

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}_d, \quad (2.9)$$

where the diffusion flux

$$\mathbf{J}_d = -M \nabla \frac{\partial g}{\partial c} \quad (2.10)$$

again follows from the free energy. From the entropy density

$$s = -\partial g / \partial T \quad (2.11)$$

we may obtain the internal energy density through a Legendre transformation

$$u = g + Ts - Pv. \quad (2.12)$$

Inserting the Fourier heat flux \mathbf{J}_q (see (3.30)), into the energy balance equation

$$\frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{J}_q \quad (2.13)$$

yields the appropriate generalization of the heat equation.

In the sequel we will supply the remaining details in the derivation of the free energy and the dynamical equations (see (5.33)–(5.35)).

3. BINARY SOLUTION, PURE PHASE

In this section we derive the free energy and the dynamical equations for a single phase binary solution. Let $G(P, T, n_i)$ be the Gibbs free energy for an equilibrium binary solution, where P is the pressure, T is the temperature, and n_i is the number of moles of the i th constituent ($i = 1, 2$). The total number of moles is $n = n_1 + n_2$. The molar concentrations are $c_i = n_i/n$. Let $c = c_1$, then $c_2 = 1 - c$. We assume that the constituents have the same density and that the pressure is constant to obviate

the need for introducing mechanics into the dynamical equations. We have the fundamental thermodynamic identities,

$$\begin{aligned} V &= \left(\frac{\partial G}{\partial P} \right)_{T, n_i} \\ S &= - \left(\frac{\partial G}{\partial T} \right)_{P, n_i} \\ \mu_i &= \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}}, \end{aligned} \quad (3.1)$$

where S is the entropy, V the volume of the system, and μ_i is the chemical potential of the i th constituent. We also define the free energy density $g(P, T, c) = G/n$, the entropy density $s = S/n$, and the molar specific volume $v = V/n$. An important difference between g and G is that the number of independent variables defining the thermodynamic state is one less for g than for G , due to the conservation law $c_1 + c_2 = 1$. This loss of a degree of freedom is a consequence of the Gibbs–Duhem equation, which gives a precise form to the physical requirement that the free energy density must be an intensive quantity, independent of the system size n . This means that thermodynamic identities involving derivatives of G with respect to the n_i cannot be directly converted to identities for g simply by dividing by n , since these identities assume that the n_i are independent, and consequently that n is not constant (in particular, it is *not* true that $\partial G/\partial n_i = \partial g/\partial c_i$). This simple point is sometimes overlooked and is the reason that derivations employing such thermodynamic identities are usually carried out with extensive variables (G, S, V) and only transformed to the corresponding densities (g, s, v) at the end. We will have to modify this approach in the next section, where the thermodynamic functions are local, depending explicitly on spatial gradients. In that case we must work with intensive variables only. The free energy for an equilibrium solution is determined by the chemical potentials μ_i and the Gibbs–Duhem identity

$$G = \sum_i n_i \mu_i. \quad (3.2)$$

In particular, the chemical potential of a pure material is identical to its Gibbs free energy density. Let μ_i^* , G_i be, respectively, the chemical potential and the free energy for the pure i th constituent in some fixed phase (so $G_i = n\mu_i^*$). For an ideal gas under isothermal conditions we have

$$dG_i = V dP = nRT dP/P = nRT d \ln(P/P_0) \quad (3.3)$$

or

$$\mu_i^*(T, P) = \mu_i^0(T) + RT \ln(P/P_0), \quad (3.4)$$

where $\mu_i^0(T)$ is the chemical potential at the reference pressure P_0 , and R is the ideal gas constant. For a condensed phase of mixed composition in equilibrium with its vapor, we define the *activity* a_i implicitly by

$$\mu_i = \mu_i^*(T, P) + RT \ln a_i. \quad (3.5)$$

An *ideal solution* satisfies

$$a_i = \frac{\text{partial pressure in vapor}}{\text{vapor pressure of pure } i} = c_i. \quad (3.6)$$

In our case P is constant and the chemical potential for the ideal solution is

$$\mu_i = \mu_i^* + RT \ln c_i. \quad (3.7)$$

The free energy density $\mu_1 c_1 + \mu_2 c_2$ for the ideal solution is then a sum

$$g_I = g_T + g_M \quad (3.8)$$

of a linear transitional term

$$g_T = \mu_1^* c_1 + \mu_2^* c_2 \quad (3.9)$$

and the free energy of mixing

$$g_M = RT(c_1 \ln c_1 + c_2 \ln c_2). \quad (3.10)$$

The latter arises from the *entropy of mixing* $s_M = g_M/T$, which is a consequence of the fact that a mixture is more disordered than its pure constituents.

The ideal solution is an overly simplistic model for a real solution, although it becomes exact in the limit $c \rightarrow 0, 1$ [43–44]. However, it is a convenient starting point due to the simple form of the chemical potentials. More realistic models are generally obtained as perturbations of the ideal solution (though the “perturbation” terms may not be small). We will fix the temperature dependence of the free energy by assuming that the heat capacity at constant volume

$$C_V(n_1, n_2) = T \frac{\partial S}{\partial T} = -T \frac{\partial^2 G}{\partial T^2} \quad (3.11)$$

is independent of temperature. This is a reasonable approximation over a moderate temperature range and can be appropriately generalized for temperature dependence for a broad range. Then we may integrate (3.11) to obtain

$$G = -C_V T \ln T + K_1(n_1, n_2) + TK_2(n_1, n_2). \quad (3.12)$$

The chemical potentials are then

$$\mu_i = -\frac{\partial C_V}{\partial n_i} T \ln T + \frac{\partial K_1}{\partial n_i} + T \frac{\partial K_2}{\partial n_i}. \quad (3.13)$$

Comparing with the previous result (3.7), we get

$$\begin{aligned}\frac{\partial C_V}{\partial n_i} &= C_{V1} = \text{const} \\ \mu_i^* &= -C_{V1} T \ln T + \frac{\partial K_1}{\partial n_i} + \xi_i T \\ \frac{\partial K_2}{\partial n_i} &= R \ln c_i + \xi_i,\end{aligned}\quad (3.14)$$

where ξ_i is a constant, and we have used $\ln c_i = \ln n_i - \ln n$. For simplicity we will assume that both constituents have the same number of microscopic degrees of freedom and that, as a consequence, C_{V1} is the same for both constituents. In fact, we will assume that the heat capacity is the same in both phases, which would be strictly true for a material with a monatomic solid state. The first and third equations in (3.14) integrate to produce

$$\begin{aligned}C_V &= C_{V0} + nC_{V1} \\ K_2 &= Rn(c_1 \ln c_1 + c_2 \ln c_2) + n(c_1 \xi_1 + c_2 \xi_2) + K_{20}\end{aligned}\quad (3.15)$$

with constants of integration C_{V0} , K_{20} . Gibbs–Duhem and (3.11) require that $C_{V0} = 0$, and that the molar-specific heat capacity $C_{V1} = C_v$ is constant. Now substituting the expression for μ_i^* into (3.9) we obtain one form of the free energy density for the ideal solution,

$$g_I = g_M - C_v T \ln T + (c_1 \xi_1 + c_2 \xi_2) T + c_1 \frac{\partial K_1}{\partial n_1} + c_2 \frac{\partial K_1}{\partial n_2}. \quad (3.16)$$

Another form of the free energy density follows from (3.12) and (3.15),

$$g_I = g_M - C_v T \ln T + (c_1 \xi_1 + c_2 \xi_2) T + K_1/n + K_{20}T/n. \quad (3.17)$$

Compatibility of (3.16), (3.17) requires $K_{20} = 0$ and

$$K_1 = n_1 \frac{\partial K_1}{\partial n_1} + n_2 \frac{\partial K_1}{\partial n_2}. \quad (3.18)$$

Note that the partial differential equation (3.18) is a form of the Gibbs–Duhem equation and implies that K_1 is a first-order homogenous function of n_1 , n_2 , so that $K_1(n_1, n_2) = nK_1(c_1, c_2)$. In addition, (3.8)–(3.9) require that g_M be the only term that is nonlinear in c_i , so we must have

$$K_1(n_1, n_2) = n(\zeta_1 c_1 + \zeta_2 c_2), \quad (3.19)$$

where ζ_i are constants. The final form of the ideal solution free energy is (3.8)–(3.9), where the free energy densities in the pure materials are

$$\mu_i^* = g_i = -C_v T \ln T + \xi_i T + \zeta_i. \quad (3.20)$$

At intermediate concentrations (c_1, c_2 not close to 0 or 1), the free energy of a real mixture exhibits stronger nonlinear interactions due to mixing than can be described by the ideal mixing energy $G_M = ng_M$. The free energy is expressed in the form $G = G_I + G_E$, where G_I is the ideal solution free energy derived above, and G_E is the *excess free energy*. We may relate G_E to the general form (3.5) of the chemical potentials by defining the *activity coefficients* $\gamma_i = a_i/c_i$, with the result:

$$G_E = RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2). \quad (3.21)$$

Since the mixture becomes ideal in the limit of a pure material, G_E must vanish when either concentration does, or

$$\lim_{c_1 \rightarrow 1} \gamma_1 = - \lim_{c_2 \rightarrow 1} \gamma_2 = 0, \quad (3.22)$$

so that $a_i \approx c_i$ close to a pure “*i*” state ($c_i \approx 1$). In addition, *Rault's law* [43] dictates that the *slopes* of the activity-concentration curves are the same in the limit of a pure material, or that

$$\lim_{c_1 \rightarrow 1} \frac{da_1}{dc} = - \lim_{c_2 \rightarrow 1} \frac{da_2}{dc} = 1, \quad (3.23)$$

which, together with (3.22), implies

$$\lim_{c_1 \rightarrow 1} \frac{d \ln \gamma_1}{dc_2} = \lim_{c_2 \rightarrow 1} \frac{d \ln \gamma_2}{dc_1} = 0. \quad (3.24)$$

The simplest form of the excess free energy that is consistent with (3.22)–(3.24) is obtained by assuming that $\ln \gamma_1 \propto c_2^2$, $\ln \gamma_2 \propto c_1^2$ with the same constant of proportionality (actually, a function of T). The result is a *regular solution* and has the form

$$G_E = n\Omega(T) c_1 c_2, \quad (3.25)$$

which provides a leading order correction (in powers of c_i) to the ideal solution and is valid for real materials over a larger concentration range. Since C_v is constant and the only permissible nonlinearity in the temperature is already incorporated in G_I , $\Omega(T)$ must be linear in T , or

$$\Omega(T) = \Omega_0 + \Omega_1 T \quad (3.26)$$

for constants Ω_0, Ω_1 . The free energy density for the regular solution then takes the form

$$g = c_1 g_1 + c_2 g_2 + g_M + \Omega c_1 c_2. \quad (3.27)$$

The chemical potentials are

$$\mu_i = \mu_i^* + \Omega(1 - c_i)^2 + RT \ln c_i \quad (3.28)$$

and the entropy density is

$$s = -\frac{\partial g}{\partial T} = C_v(1 + \ln T) - \Omega_1 c_1 c_2 - \xi_1 c_1 - \xi_2 c_2 + s_M. \quad (3.29)$$

The non-equilibrium dynamics of the single phase binary system may now be introduced employing standard theory [45–46]. We assume that the heat flux has the Fourier form

$$\mathbf{J}_q = -k \nabla T \quad (3.30)$$

(where we neglect the Dufour cross effect, i.e., the transport of heat by mass diffusion). The total diffusion flux has the form

$$\mathbf{J}_d = -M \nabla(\mu_1 - \mu_2). \quad (3.31)$$

The diffusion equation is then

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}_d = \nabla M \cdot \nabla(\mu_1 - \mu_2), \quad (3.32)$$

where the *mobility* M is in general a function of the local thermodynamic state. The simplest form producing the correct behavior in the limit of a pure material is $M = Dc(1 - c)$, where D is the *binary diffusion coefficient* D (see discussion by Hilliard [50]). The energy balance equation, or the first law of thermodynamics, is (in the absence of $P dV$ work contributions)

$$\frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{J}_u, \quad (3.33)$$

where the internal energy density

$$u = C_v T + c \zeta_1 + (1 - c) \zeta_2 + \Omega_0 c(1 - c) - Pv \quad (3.34)$$

follows from (3.29) and the Legendre transformation

$$u = g + Ts - Pv.$$

The energy flux \mathbf{J}_u is the same as the heat flux \mathbf{J}_q in this case. In the absence of work, energy is transported by heat flow alone. Substituting (3.30) and (3.34) into (3.33), one has the heat equation

$$C_v \frac{\partial T}{\partial t} + \left(\zeta_1 - \zeta_2 + \frac{\partial}{\partial c} u_E(T, c) \right) \frac{\partial c}{\partial t} = \nabla \cdot k \nabla T, \quad (3.35)$$

where $\zeta_1 - \zeta_2$ is the difference in internal energy density between the two pure materials and

$$u_E = g_E - T \frac{\partial g_E}{\partial T} - Pv = \Omega_0 c(1-c) - Pv \quad (3.36)$$

is the excess internal energy density. Note that if $\Omega_0 = 0$ and $\zeta_1 = \zeta_2$ we obtain the standard form of the heat equation. Define

$$\mu_c \equiv \frac{\partial g(T, c)}{\partial c} = \mu_1 - \mu_2 = g_1 - g_2 + RT \ln \frac{c}{1-c} + \frac{\partial g_E(T, c)}{\partial c}. \quad (3.37)$$

Now differentiating the entropy density (3.29) and using (3.32), (3.35) one obtains

$$\frac{\partial s}{\partial t} = \frac{\nabla \cdot k \nabla T}{T} - \frac{\mu_c \nabla \cdot M \nabla \mu_c}{T}.$$

After applying some standard vector identities, this becomes

$$\frac{\partial s}{\partial t} = -\nabla \cdot \mathbf{J}_s + \theta \quad (3.38)$$

where the *entropy flux* \mathbf{J}_s is

$$\mathbf{J}_s = -\frac{k}{T} \nabla T + \frac{M \mu_c}{T} \nabla \mu_c \quad (3.39)$$

and the *entropy source* θ is

$$\theta = \frac{k}{T^2} |\nabla T|^2 - \frac{M \mu_c}{T^2} \nabla \mu_c \cdot \nabla T + \frac{M}{T} |\nabla \mu_c|^2. \quad (3.40)$$

A change dS in the total entropy of a volume V may be decomposed into changes dS_{ext} due to fluxes through the boundary of V plus changes dS_{int} due to local entropy production. The total entropy rate is then the sum of

$$\frac{dS_{\text{int}}}{dt} = \rho \iiint_V \theta dV \quad (3.41)$$

and

$$\frac{dS_{\text{ext}}}{dt} = \rho \iiint_V \nabla \cdot \mathbf{J}_s dV = -\rho \iint_{\partial V} \mathbf{n} \cdot \mathbf{J}_s dA, \quad (3.42)$$

where ρ is the molar density of the material. The second law of thermodynamics requires that the entropy source be positive semi-definite. Since (3.40) is a quadratic

form in ∇T , $\nabla \mu_c$, we have (along with $k \geq 0$, $M \geq 0$) the necessary and sufficient condition

$$kT - \frac{M}{4} \mu_c^2 \geq 0 \quad (3.43)$$

for the validity of the second law for all processes. For small c , the condition is (to leading order in c)

$$kT - \frac{Dc}{4} (RT \ln c)^2 \geq 0 \quad (3.44)$$

and is automatically satisfied for sufficiently small c . At intermediate concentrations, (3.43) places a nontrivial constraint on the material parameters.

4. PHASE FIELD EQUATIONS FOR A PURE MATERIAL

In the previous section we observed that a knowledge of the equilibrium free energy for the binary solution enabled us to construct the non-equilibrium evolution equations. In this classical approach to non-equilibrium thermodynamics, spatial inhomogeneity is introduced only through the phenomenological fluxes. Our purpose in the present section is to demonstrate how phenomenological non-equilibrium thermodynamics may be generalized in a consistent way to incorporate spatial inhomogeneity into the free energy. This will enable us to incorporate more general physics, such as diffusion, into the phase field equations without the necessity of modeling the microscopic physics and taking the thermodynamic limit. This has substantial practical significance, since a derivation from first principles may not be tractable for more general materials. However, as phenomenological non-equilibrium thermodynamics is not a completely general theory, it is important in any new application to ensure that the formalism is consistent with microscopic physics to the extent possible (i.e., mathematical consistency alone is not sufficient). In our case, we have the derivation of the standard phase field equation as our connection with first principles [14]. On the other hand, the non-equilibrium thermodynamics of a two-component material follows the well-established path of the previous section. In this section we will obtain a thermodynamically consistent form of the phase field equations, which will refine the temperature dependence in the standard equations (1.4), (1.5). In the following section we will combine the results of Sections 3 and 4 to derive phase field equations for a two-phase binary solution.

In formulating the problem, it is useful to observe the close analogy between the phase field equation and a reaction rate equation for a single exothermic reaction, with the order parameter corresponding to a reaction progress variable and the latent heat corresponding to an exothermic heat release. Typically, a reaction progress variable may be the mole fraction or concentration of a reactant and controls the release of heat via a linear term in the internal energy. For a solid-liquid transition in a metal in the non-critical regime, the thickness of the interphase region is at most on the order of a few tens of atomic spacings, and it is not strictly

correct to interpret the order parameter as the concentration of one phase, although this interpretation may be a useful heuristic device.

Landau free energies of the type we are considering have been derived from first principles and used to calculate quantitative phase diagrams [47]. This can be done, for example, by expanding the free energy of the solid in powers of the density of defects. The resulting free energy achieves a second minimum where the defect density saturates, which defines the liquid phase. We may assume that the order parameter is linearly related to the density of defects in the solid state. The order parameter may be normalized so that, in equilibrium and at the melting temperature, the free energy minima corresponding to the solid or liquid state occur when the order parameter is 0 or 1, respectively. In this context, a "defect" means a hole in the partially formed lattice which may be occupied by molecules possessing the energy of the liquid state (i.e., which are not yet bonded to the lattice). This leads to a macroscopic interpretation of the order parameter as essentially the (mass or mole) density of the liquid phase. It is important to note here that, in general, we can only hope to impose this convenient normalization at the coexistence curve, and that the pure solid and liquid phases will not always occur at the values 0 and 1. While it may be possible to force the order parameter to always have these fixed values at the free energy minima by the introduction of additional nonlinearities into the free energy, the additional terms are inconsistent with the microscopic interpretation of the order parameter (the saturation point for the defect density is temperature and pressure dependent), and introduce artificial nonlinearity into the equations. From a phenomenological perspective, this additional nonlinearity contributes to the latent heat deposition term in the internal energy (see (4.11)). This is very counterintuitive. For an exothermic reaction, the heat deposition is necessarily linear since a fixed quantity of heat is released by each set of reacting molecules. The situation for a first-order phase transition is similar, since each molecule changing phase is expected to release (or absorb) a fixed amount of the latent heat. Thus there is no physical basis for expecting latent heat to be deposited nonlinearly. Furthermore, in any realistic system involving pressure and density differences, for example, the order parameter will not be fixed in the pure phase. We must conclude then, that fixing the phases at 0 and 1 is inconsistent with the physics of first order phase transitions from both a microscopic and a phenomenological perspective. This point has caused some confusion in the literature and has led some to claim that these additional nonlinearities are necessary for "thermodynamic consistency." This is incorrect. The pure phases are *defined* by the free energy minima, and not by an ad-hoc imposed value on the order parameter. Nevertheless, models with the free energy minima fixed in this manner may be convenient for the purposes of mathematical theorems [32] and numerical computation, as long as artifacts of the additional nonlinearity are avoided [23, 25, 26].

The most general form of the Gibbs free energy density consistent with constant specific volume, pressure, and specific heat capacity is

$$g = -C_v T \ln T + f_0[\phi] + f_1[\phi] T, \quad (4.1)$$

where f_0, f_1 are functionals of the order parameter ϕ . The entropy density is

$$s = -\frac{\partial g}{\partial T} = C_v(1 + \ln T) - f_1. \quad (4.2)$$

The internal energy density

$$u = C_v T + f_0 - Pv \quad (4.3)$$

is then defined by the Legendre transformation as before. The chemical potential conjugate to ϕ is defined analogously to (2.3), but with the partial derivative with respect to ϕ replaced by a variational derivative. The total free energy in a volume V is given by

$$\mathcal{G}[\phi] = \rho \iiint_V g \, dV. \quad (4.4)$$

The Frechet derivative

$$(D\mathcal{G}[\phi])[\eta] = \left. \frac{d}{d\varepsilon} \mathcal{G}[\phi + \varepsilon\eta] \right|_{\varepsilon=0} \quad (4.5)$$

of \mathcal{G} with respect to ϕ may, after integration by parts, be expressed in the form

$$(D\mathcal{G}[\phi])[\eta] = \rho \iiint_V \mu \eta \, dV + \rho \iint_{\partial V} \mathbf{n} \cdot \mathbf{J}_\phi \eta \, dA,$$

where \mathbf{J}_ϕ represents the change in the free energy due to boundary fluxes. By allowing η to vanish on ∂V , the boundary term may be made to vanish. We will see that the factor μ in the remaining volume integral is the difference in the local chemical potentials of the two phases. In equilibrium, we must have $(D\mathcal{G}[\phi])[\eta] = 0$ for all η and all V , which implies that μ must vanish identically. Note that if the material is spatially homogenous, then (using $V\rho = n$) we have $\mathcal{G} = gn = G$. Also, $\mathbf{J}_\phi = 0$, and $\mu = \partial g / \partial \phi$.

To illustrate the usefulness of the chemical reaction analogy, we show that for a homogenous material in equilibrium with two coexisting phases, μ is the difference in the local chemical potentials for the two phases if ϕ is interpreted as the mole fraction of one phase. Let n^l, n^s be the number of moles of liquid, solid, respectively, and let $\phi^l = n^l/n, \phi^s = n^s/n$ be the corresponding mole fractions, where $n = n^l + n^s$. The chemical potentials for the two phases are

$$\begin{aligned} \mu^l &= \frac{\partial G}{\partial n^l} = \bar{g} + \left(\frac{\partial \bar{g}}{\partial \phi^l} - \frac{\partial \bar{g}}{\partial \phi^s} \right) \phi^s \\ \mu^s &= \frac{\partial G}{\partial n^s} = \bar{g} - \left(\frac{\partial \bar{g}}{\partial \phi^l} - \frac{\partial \bar{g}}{\partial \phi^s} \right) \phi^l, \end{aligned} \quad (4.6)$$

where

$$\bar{g}(\phi', \phi^s, T) \equiv G(n', n^s, T)/n. \quad (4.7)$$

Then, setting $\phi' = \phi$, $\phi^s = 1 - \phi$, we have

$$\begin{aligned} g(\phi, T) &\equiv \bar{g}(\phi, 1 - \phi, T) \\ \mu &= \frac{\partial g}{\partial \phi} = \left(\frac{\partial \bar{g}}{\partial \phi'} - \frac{\partial \bar{g}}{\partial \phi^s} \right) = \mu' - \mu^s, \end{aligned} \quad (4.8)$$

proving the assertion. We see that the equilibrium condition $\mu = 0$ of the Landau–Ginzburg theory reduces to the usual condition $\mu' = \mu^s$ for local equilibrium in a two-component system. The non-equilibrium dynamics of the transition is then governed by

$$\tau \frac{\partial \phi}{\partial t} = -\mu,$$

where τ is the relaxation parameter. To obtain the non-local version of the equilibrium conditions (with the chemical potentials evaluated in the separate phases, and equality holding across the interface), one would have to define the pure phase values of the chemical potentials on either side of the diffuse interface. In a one-dimensional geometry, the values at $\pm \infty$ could be used. This is essentially what is done in Section 6, where the matching conditions (6.19) are just the non-local equilibrium conditions defining the ideal phase diagram.

The functionals f_0, f_1 in (4.1) must be chosen to ensure that the first and second laws of thermodynamics are satisfied. Local energy conservation is expressed by (3.33) as before. We may satisfy (3.33) while conforming to (1.4)–(1.5) as closely as possible by choosing

$$\begin{aligned} f_0 &= 2\beta T_m \phi \\ f_1 &= \frac{B}{2} |\nabla \phi|^2 + \frac{\alpha}{4} \phi^2 (1 - \phi)^2 - 2\beta \phi, \end{aligned} \quad (4.9)$$

where T_m is the equilibrium melting temperature. Inserting f_0, f_1 into the definitions above yields the entropy density

$$s = C_v (1 + \ln T) - \frac{B}{2} |\nabla \phi|^2 - \frac{\alpha}{4} \phi^2 (1 - \phi)^2 + 2\beta \phi, \quad (4.10)$$

the internal energy density,

$$u = C_v T + 2\beta T_m \phi - P v, \quad (4.11)$$

and the chemical potential,

$$\mu = -\nabla \cdot B T \nabla \phi + \alpha T \phi (1 - \phi) (1/2 - \phi) - 2\beta (T - T_m).$$

One of the logical subtleties of phenomenological non-equilibrium thermodynamics is in the manner that the dynamical equations are obtained in boot-strap fashion from the equilibrium equations. This is not a serious problem when the equilibrium state is constant in both space and time (thermostatics), since the dependence of the free energy, internal energy, etc., on the state variables is purely algebraic. In the present case, the equilibrium (i.e., time-independent) system is inhomogenous in space, and the free energy depends explicitly on the spatial gradient $\nabla\phi$. Since we require $T = \text{constant}$ in equilibrium, this leads to some arbitrariness in the placement of the temperature factor in the $\nabla\phi$ term of μ . We will show below that the choice

$$\mu = -T\nabla \cdot B\nabla\phi + \alpha\phi(1-\phi)(1/2-\phi) - 2\beta(T-T_m) \quad (4.12)$$

enables us to formally satisfy the second law of thermodynamics. This is along the lines of the philosophical approach taken in [19]. An alternative approach is to include the $|\nabla\phi|^2$ term in f_0 rather than f_1 as was done in [15, 20]. The difficulty with the temperature factor in (4.12) then does not arise. This has the effect of incorporating terms involving $\nabla\phi$ in the internal energy and consequently in the latent heat deposition (and removing these gradient dependencies from the entropy). This significantly complicates the physical interpretation of the equations. It is also counterintuitive, since the dissipative $|\nabla\phi|^2$ term is evidently entropy producing. A satisfactory resolution of this question will undoubtedly require a direct appeal to first principles and is beyond the scope of this paper. The heat equation

$$C_v \frac{\partial T}{\partial t} + 2\beta T_m \frac{\partial \phi}{\partial t} = \nabla \cdot k \nabla T \quad (4.13)$$

follows from (3.33) and (4.11). The phase equation is

$$\tau \frac{\partial \phi}{\partial t} = T\nabla \cdot B\nabla\phi - \alpha\phi(1-\phi)(1/2-\phi) + 2\beta(T-T_m), \quad (4.14)$$

where we must have $A > 0$ for the phase equilibria to be stable. As before, we compute the entropy rate $\partial s / \partial t$ from (4.10). After applying vector identities, we get

$$\frac{\partial s}{\partial t} = -\nabla \cdot \mathbf{J}_s + \theta, \quad (4.15)$$

where the entropy flux is

$$\mathbf{J}_s = \frac{k}{T} \nabla T + \frac{B\mu}{\tau} \nabla\phi \quad (4.16)$$

and the entropy source,

$$\theta = k \left| \frac{\nabla T}{T} \right|^2 + \frac{\mu^2}{\tau T}, \quad (4.17)$$

is positive definite.

5. PHASE FIELD EQUATION FOR A REGULAR BINARY SOLUTION

Consider first a two-phase regular binary solution in phase equilibrium. The free energy density in each phase is assumed to have the form

$$\begin{aligned} g^l &= c_1 g_1^l + c_2 g_2^l + g_M + \Omega c_1 c_2 \\ g^s &= c_1 g_1^s + c_2 g_2^s + g_M + \Omega c_1 c_2, \end{aligned} \quad (5.1)$$

where

$$g_M = RT(c_1 \ln c_1 + c_2 \ln c_2) \quad (5.2)$$

are the mixing energies;

$$g_i^{l/s} = -C_v T \ln T + \zeta_i^{l/s} T + \zeta_i^{l/s} \quad (5.3)$$

are the free energies of the pure constituents in each phase. The chemical potentials are

$$\mu_i^{l/s} = g_i^{l/s} RT \ln c_i + \Omega(1 - c_i)^2. \quad (5.4)$$

The entropy densities are

$$s^{l/s} = c_1 s_1^{l/s} + c_2 s_2^{l/s} + s_M + s_E, \quad (5.5)$$

where the pure material, mixing, and excess entropies are

$$s_i^{l/s} = C_v(1 + \ln T) - \zeta_i^{l/s} \quad (5.6)$$

$$s_M = -R(c_1 \ln c_1 + c_2 \ln c_2) \quad (5.7)$$

$$s_E = -\Omega_1 c_1 c_2. \quad (5.8)$$

The internal energy densities are then

$$u^{l/s} = c_1 u_1^{l/s} + c_2 u_2^{l/s} + u_E, \quad (5.9)$$

where

$$u_i^{l/s} = C_v T + \zeta_i^{l/s} - Pv \quad (5.10)$$

$$u_E = \Omega_0 c_1 c_2. \quad (5.11)$$

We have assumed, for simplicity, that C_v is independent of material and phase. This assumption is valid for materials for which both phases have the same number of microscopic vibrational degrees of freedom and it is expected to be at least qualitatively reasonable for some more general transitions. Since we are mainly interested in the small c regime, we have also assumed that Ω_0 and Ω_1 are independent of material and phase, consistent with the "perturbative" nature of the excess free energy.

The conditions for equilibrium of the two-phase system are $T = \text{constant}$, and the pair of conditions $\mu_i^l = \mu_i^s$. We define

$$[X]_{\text{eq}} \equiv X^l(c_1^l, c_2^l) - X^s(c_1^s, c_2^s), \quad (5.12)$$

where $c_i^{l/s}$ are the mole fractions of each constituent in the liquid and solid phases, respectively, in a binary system in phase equilibrium. From (5.4) the equilibrium conditions may be expressed as

$$[\mu_1]_{\text{eq}} = [g_1]_{\text{eq}} + RT \ln \frac{c_1^l}{c_1^s} + \Omega[(1-c)^2]_{\text{eq}} = 0 \quad (5.13a)$$

$$[\mu_2]_{\text{eq}} = [g_2]_{\text{eq}} + RT \ln \frac{1-c_1^l}{1-c_1^s} + \Omega[c^2]_{\text{eq}} = 0, \quad (5.13b)$$

where $c_1^{l/s} = c^{l/s}$, $c_2^{l/s} = 1 - c^{l/s}$. The jump in the entropy density follows from (5.5) and must satisfy

$$[s]_{\text{eq}} = -\Omega_1[c_1 c_2]_{\text{eq}} - [\xi_1 c_1 + \xi_2 c_2]_{\text{eq}} - R[c_1 \ln c_1 + c_2 \ln c_2]_{\text{eq}} > 0.$$

Equations (5.13a), (5.13b) are a system of two equations in the three unknowns c^l , c^s , T , and thus define a one-dimensional manifold. An important interest is the behavior of this manifold for small c^l , c^s . We see immediately from (5.13a) that $c^l \rightarrow 0$ as $c^s \rightarrow 0$. If we eliminate c^s , we obtain the equation of the *liquidus curve* $c^l(T)$. Alternatively, we could eliminate c^l to obtain the *solidus curve* $c^s(T)$. These eliminations can be carried out exactly for the ideal solution ($\Omega = 0$), with the result:

$$c^l = \frac{1 - \exp([g_2]_{\text{eq}}/RT)}{\exp([g_1]_{\text{eq}}/RT) - \exp([g_2]_{\text{eq}}/RT)} \quad (5.14a)$$

$$c^s = \frac{(1 - \exp([g_2]_{\text{eq}}/RT)) \exp([g_1]_{\text{eq}}/RT)}{\exp([g_1]_{\text{eq}}/RT) - \exp([g_2]_{\text{eq}}/RT)}. \quad (5.14b)$$

The ideal solution phase diagram is shown in Fig. 2. Between the liquidus and solidus curves is the phase coexistence region. This region is one of the principle distinguishing features of multicomponent phase diagrams.

For the regular solution, the phase diagram is qualitatively similar to the ideal solution when the concentrations are close to 0 or 1 (Rault's law), with the liquidus and solidus curves meeting at the melting temperatures T_i of the pure constituents. When Ω_0 , Ω_1 are sufficiently large, the liquidus and solidus curves undergo qualitative changes. Then, the excess contributions in (5.13) dominate the behavior at intermediate concentrations. This competition between small concentrations of ideal behavior and the strong mixing interaction at intermediate concentrations may produce singularities and topological changes in the liquidus and solidus. These non-linear effects have important implications for existence and uniqueness of solutions to the dynamical equations derived below.

Denote the (constant) pure constituent equilibrium variables by an overbar. Thus one has

$$\bar{s}_1^{l/s} \equiv s_1^{l/s}|_{c=1} \quad (5.15a)$$

$$\bar{s}_2^{l/s} \equiv s_2^{l/s}|_{c=0} \quad (5.15b)$$

and similarly for u, g . Evaluating (5.15a), (5.15b) in the limit of zero and unity concentrations, respectively, gives

$$\xi_i^{l/s} = C_v(1 + \ln T_i) - \bar{s}_i^{l/s} \quad (5.16a)$$

$$\zeta_i^{l/s} = \bar{u}_i^{l/s} - C_v T_i + Pv; \quad (5.16b)$$

then (5.3) yields

$$\bar{g}_i^{l/s} = \bar{u}_i^{l/s} - \bar{s}_i^{l/s} T_i + Pv. \quad (5.17)$$

We can then eliminate the eight constants $\xi_i^{l/s}, \zeta_i^{l/s}$ in favor of the more physically transparent parameters $\bar{s}_i^{l/s}, \bar{u}_i^{l/s}$. In particular, we have from (5.6) and (5.16)

$$[s_i]_{\text{eq}} = [\bar{s}_i]_{\text{eq}} = -[\xi_i]_{\text{eq}}, \quad (5.18a)$$

$$[u_i]_{\text{eq}} = [\bar{u}_i]_{\text{eq}} = [\zeta_i]_{\text{eq}}. \quad (5.18b)$$

Using these in (5.17) yields

$$[\bar{g}_i]_{\text{eq}} = [\xi_i]_{\text{eq}} T_i + [\zeta_i]_{\text{eq}} = [\bar{u}_i]_{\text{eq}} - T_i [\bar{s}_i]_{\text{eq}} = 0 \quad (5.19)$$

which expresses equality of the free energies for the two-phase pure materials. Expressing (5.3), (5.6), (5.10) in the barred variables then gives the final form of the pure material, single phase potentials,

$$g_i^{l/s} = \bar{g}_i^{l/s} + (C_v - \bar{s}_i^{l/s})(T - T_i) - C_v T \ln(T/T_i) \quad (5.20)$$

$$s_i^{l/s} = \bar{s}_i^{l/s} + C_v \ln(T/T_i) \quad (5.21)$$

$$u_i^{l/s} = \bar{u}_i^{l/s} + C_v(T - T_i). \quad (5.22)$$

We now introduce an order parameter ϕ into the free energy for the binary solution. We will assume that all non-linear contributions (in ϕ, c) have been accounted for in (4.1), (5.1). The material parameters will thus be assumed to undergo a linear transition (in ϕ) from \bar{s}_i^l, \bar{u}_i^l in the liquid phase to \bar{s}_i^s, \bar{u}_i^s in the solid phase. The definition

$$g_0 \equiv \phi g^l + (1 - \phi) g^s \quad (5.23)$$

yields the following free energy for the two phase binary alloy (Fig. 1):

$$g = g_0 + \frac{B}{2} T |\nabla \phi|^2 + \frac{\alpha}{4} T \phi^2 (1 - \phi)^2. \quad (5.24)$$

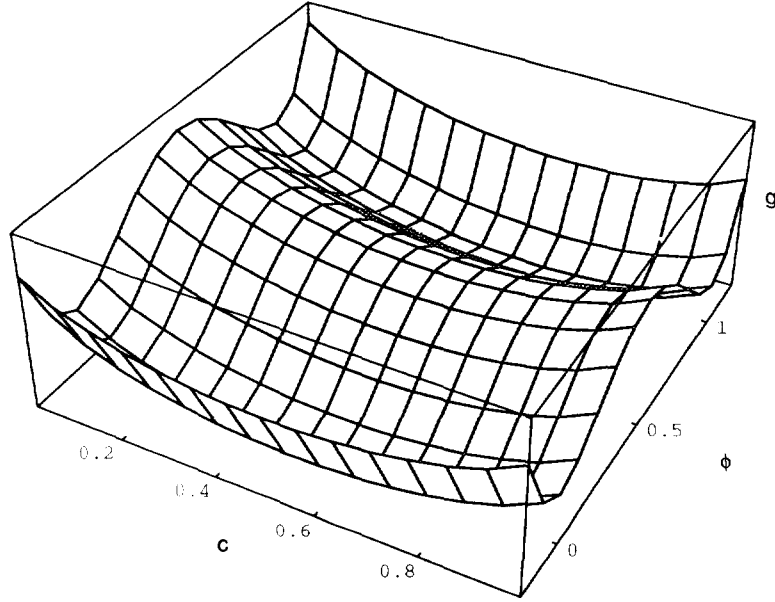


FIG. 1. The free energy as a function of concentration and order parameter at a fixed temperature. There are exactly two local minima corresponding to the two distinct phases. Phase coexistence occurs when the free energy has the same value at both minima.

Define the transition functions

$$\bar{s}^{l/s}(c) \equiv c_1 \bar{s}_1^{l/s} + c_2 \bar{s}_2^{l/s} \quad (5.25)$$

$$\bar{u}^{l/s}(c) \equiv c_1 \bar{u}_1^{l/s} + c_2 \bar{u}_2^{l/s} \quad (5.26)$$

$$[\bar{u}]_{\text{eq}} = \bar{u}^l - \bar{u}^s = c_1 [\bar{u}_1]_{\text{eq}} + c_2 [\bar{u}_2]_{\text{eq}} \quad (5.27)$$

$$T_a(c) \equiv c_1 T_1 + c_2 T_2 \quad (5.28)$$

$$T_b(c) \equiv T_1^{c_1} T_2^{c_2}.$$

The entropy density is

$$s = -\frac{\partial g}{\partial T} = s_0 - \frac{B}{2} |\nabla \phi|^2 + \frac{\alpha}{4} \phi^2 (1 - \phi)^2, \quad (5.29)$$

where

$$s_0 = -\frac{\partial g_0}{\partial T} = \phi s^l + (1 - \phi) s^s = \phi \bar{s}^l + (1 - \phi) \bar{s}^s + C_v \ln(T/T_b) + s_M + s_E \quad (5.30)$$

The internal energy density is

$$u_0 = g_0 + Ts_0 - Pv = \phi u^l + (1 - \phi) u^s \quad (5.31)$$

$$= \phi \bar{u}^l + (1 - \phi) \bar{u}^s + C_v(T - T_a) + u_E. \quad (5.32)$$

The phase, heat, and diffusion equations now follow as before,

$$\tau \frac{\partial \phi}{\partial t} = T \nabla \cdot B \nabla \phi - \alpha T \phi (1 - \phi) (1/2 - \phi) - (g^l - g^s) \quad (5.33)$$

$$\frac{\partial u}{\partial t} = C_v \frac{\partial T}{\partial t} + [\bar{u}]_{\text{eq}} \frac{\partial \phi}{\partial t} + \frac{\partial u_0}{\partial c} \frac{\partial c}{\partial t} = \nabla \cdot k \nabla T \quad (5.34)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot Dc(1 - c) \nabla \frac{\partial g_0}{\partial c}, \quad (5.35)$$

where

$$g^l - g^s = -[\bar{s}]_{\text{eq}} T \quad (5.36)$$

$$[\bar{s}]_{\text{eq}} = \bar{s}^l - \bar{s}^s. \quad (5.37)$$

6. BASIC ASYMPTOTICS AND THE EQUILIBRIUM DIAGRAM

In this section we present the main ideas of the transition layers involved in the concentration and phase using the the methods of [42]. We defer a thorough asymptotic analysis until the next section in order to focus on the basic ideas with a minimum of technical detail and to derive the phase diagrams from our equations so that macroscopic and microscopic parameters in the equations are related to those of the phase diagram.

For convenience, we define the rescaled phase variable, ψ , the interface thickness, ε , and the surface tension, σ , by

$$\psi := 2\phi - 1, \quad \varepsilon := \left(\frac{2B}{\alpha}\right)^{1/2}, \quad \sigma := \frac{1}{12} T(2B\alpha)^{1/2}, \quad q(T) := \frac{\tau}{BT}. \quad (6.1)$$

Using the notation

$$[q_i]_{\text{eq}} := q_i^{\text{liquid}} - q_i^{\text{solid}}, \quad [q_i]_{1,2} := q_2 - q_1, \quad \langle q_i \rangle_{\text{eq}} := \frac{1}{2}(q_i^{\text{liquid}} + q_i^{\text{solid}}), \quad (6.2)$$

we can rewrite Eqs. (5.33)–(5.35) as

$$q(T) \varepsilon^2 \psi_t = \varepsilon^2 \Delta \psi + \frac{1}{2} (\psi - \psi^3) + \frac{\varepsilon}{3\sigma(T)} \{ -c [[s_i]_{\text{eq}} (T - T_i)]_{1,2} + [s_2]_{\text{eq}} (T - T_2) \} \quad (6.3)$$

$$\begin{aligned}
 & C_v T_i + \{[s_2]_{\text{eq}} T_2 - c[[s_i]_{\text{eq}} T_i]_{1,2}\} \frac{\psi_i}{2} + \{[C_v T_i - \bar{g}_i]_{1,2} - [\langle s_i \rangle_{\text{eq}} T_i]_{1,2} \\
 & - \frac{\psi}{2} [[s_i]_{\text{eq}} T_i]_{1,2} + \Omega_0(1-2c)\} c_i = \nabla \cdot k \nabla T
 \end{aligned} \tag{6.4}$$

$$\begin{aligned}
 c_i = \nabla D c(1-c) \nabla \left\{ \frac{\psi}{2} [[s_i]_{\text{eq}} (T - T_i)]_{1,2} + \frac{T}{2} [\langle s_i \rangle_{\text{eq}}]_{1,2} \right. \\
 \left. + (\Omega_0 + \Omega_1 T)(1-2c) + RT \ln \frac{c}{1-c} + C_v T \ln \frac{T_1}{T_2} \right\}.
 \end{aligned} \tag{6.5}$$

We note that σ corresponds to the leading order surface tension with a local interpretation of the definition

$$\sigma = \frac{\mathcal{F} \{ \text{with interface} \} - \frac{1}{2} \mathcal{F} \{ \text{pure liquid} \} - \frac{1}{2} \mathcal{F} \{ \text{pure solid} \}}{\text{area of interface}}. \tag{6.6}$$

The derivation of σ in the form (6.1) using (6.6) is exactly the same as the pure case, except for the factor of T which multiplies the gradient and double well terms. Note that since the surface tension is an equilibrium quantity, T is a constant T_0 in the calculation of (6.6).

For the remainder of this section we consider an alloy or mixture in equilibrium at a fixed temperature T . Initially, we assume an ideal mixture, so that $\Omega_0 = \Omega_1 = 0$. In this important special case, some key interfacial relationships can be obtained in closed form.

Let r be the coordinate which measures the distance from the interface, which is now represented as the set of points where $\psi = 0$. Using the *stretched* or *inner* coordinate, $z := r/\varepsilon$, we define

$$\hat{\psi}(z, t) := \psi(x, t), \quad \hat{c}(z, t) = c(x, t), \quad \hat{T} = T = \text{const}. \tag{6.7}$$

Then the phase equation (6.3) can be written for planar equilibrium as

$$0 = \hat{\psi}_{zz} + \frac{1}{2} (\hat{\psi} - \hat{\psi}^3) + \frac{\varepsilon}{3\sigma} \{ -\hat{c}[[s_i]_{\text{eq}} (T - T_i)]_{1,2} + [s_2](T - T_2) \}. \tag{6.8}$$

We look for an asymptotic solution of the form

$$\hat{\psi} = \hat{\psi}^0 + \varepsilon \hat{\psi}^1 + \varepsilon^2 \hat{\psi}^2 + \dots \tag{6.9}$$

and similarly for the other variables, so that substituting this identity into (6.8) and formally equating terms with similar powers of ε leads to the $O(1)$ equation,

$$\hat{\psi}_{zz}^0 + \frac{1}{2} (\hat{\psi}^0 - \hat{\psi}^0)^3 = 0. \tag{6.10}$$

This has a solution $\hat{\psi}^0(z) = \tanh z/2$. (We assume boundary conditions of solid on the left and liquid on the right, so that $\hat{\psi}(\pm\infty) = \pm 1$.)

Next, we consider the concentration equation (6.5). A stationary concentration profile is described by setting $\nabla \partial g / \partial c$ to zero in (5.35) or (6.5). Note that this is equivalent to setting the diffusion flux to zero (3.31). Although it is also possible to consider more general solutions, e.g., by simply setting the time derivative equal to zero in (6.5), seeking stationary solutions of the form $\partial g / \partial c = 0$ (i.e., without the gradient) leads to an over-determined system which implies a particular temperature at the boundary (this point will be discussed in greater detail later in this section under the subheading “the concentration profile”).

Using the notation

$$N(T) := \frac{1}{2} [[s_i]_{\text{eq}} (T - T_i)]_{1,2}, \quad (6.11)$$

one can rewrite the no-flux equilibrium equation $\nabla \partial g / \partial c = 0$ as

$$\left(N\hat{\psi}^0 + RT \ln \frac{\hat{c}^0}{1 - \hat{c}^0} \right)_z = 0 \quad \text{or} \quad \hat{\psi}_z^0 = -\frac{RT}{N} \frac{\hat{c}_z^0}{\hat{c}^0(1 - \hat{c}^0)}. \quad (6.12)$$

Integration of (6.12) with respect to z implies that

$$N\hat{\psi}^0 + RT \ln \frac{\hat{c}^0}{1 - \hat{c}^0} = A, \quad (6.13)$$

where A is independent of z but may depend on other variables, such as temperature (discussed in detail later in this section). We subtract (6.13) evaluated at $z = -\infty$ from the same equation at $z = +\infty$. Using the notation $[q]_{\pm}^{\pm} := \lim_{r \rightarrow 0_{\pm}} q$ and the standard asymptotic matching result that $\lim_{z \rightarrow \pm\infty} \hat{c}^0 = \lim_{r \rightarrow 0_{\pm}} \hat{c}^0$, we obtain to leading order

$$\left[\ln \frac{c}{1 - c} \right]_{-}^{+} = -\frac{2N}{RT}. \quad (6.14)$$

Thus, (6.14) is one of the equations which relate the values of concentration on the liquid and solid sides of the interface, c^+ and c^- , to the temperature T^0 on the interface. Upon deriving a second relation using the phase equation (6.3), we will be able to construct the liquidus and solidus lines of the equilibrium phase diagram. The basic theory of simple one-phase sharp interface models is discussed in [46]. Subtracting the $O(1)$ equation (6.10) from the full equation (6.8), one has the $O(\varepsilon)$ equation:

$$\mathcal{L}\hat{\psi}^1 := \hat{\psi}_{zz}^1 + \frac{1}{2}(1 - 3(\hat{\psi}^0)^2)\hat{\psi}^1 = -\frac{1}{3\sigma} \{ -2N\hat{c}^0 + [s_2](T_0 - T_2) \} =: H. \quad (6.15)$$

Since $\hat{\psi}_z^0$ is a solution to the homogeneous equation $\mathcal{L}\eta=0$, the Fredholm alternative theorem implies that a necessary condition for the solvability of (6.15) is that $\hat{\psi}_z^0$ be orthogonal to H , i.e.,

$$\int_{-\infty}^{\infty} \hat{\psi}^0 \{ -2N\hat{c}^0 + [s_2]_{\text{eq}} (T - T_2) \} dz = 0. \tag{6.16}$$

(Note that in this special case, Fredholm's alternative is obtained simply by differentiating (6.10) and multiplying by $\hat{\psi}^1$ and subtracting from it (6.15) multiplied by $\hat{\psi}_z^0$. Then (6.16) is obtained upon integration by parts using the boundary conditions $\hat{\psi}_z^0(\pm\infty)=0$.) Equation (6.16) can be evaluated using (6.12) and $\int_{-\infty}^{\infty} \hat{\psi}_z^0 dz = 2$ as

$$2[s_2]_{\text{eq}} (T - T_2) = 2N \int_{-\infty}^{\infty} \frac{RT}{N} \frac{\hat{c}_z^0}{1 - \hat{c}^0} dz = 2RT \ln(1 - \hat{c}^0(z)) \Big|_{-\infty}^{\infty}. \tag{6.17}$$

Using the matching condition $\lim_{z \rightarrow \pm\infty} \hat{c}^0 = \lim_{r \rightarrow 0 \pm} c^0$ again, (6.17) has the form

$$1 - \frac{T_2}{T} = \frac{R}{[s_2]_{\text{eq}}} \ln \left(\frac{1 - c^+}{1 - c^-} \right). \tag{6.18}$$

We now have two relations, (6.14) and (6.18) for c^+ , c^- , and T_0 . This determines the phase diagram (Fig. 2), since the solidus $c^-(T)$ and liquidus $c^+(T)$ can be determined as a function of T as a consequence of the following simple computation.

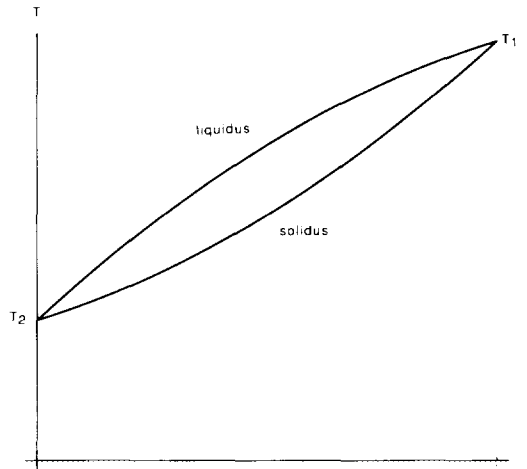


FIG. 2. The phase diagram for an ideal solution, exhibiting the characteristic phase coexistence region bounded by the liquidus and solidus curves, in the case where $T_1 > T_2$.

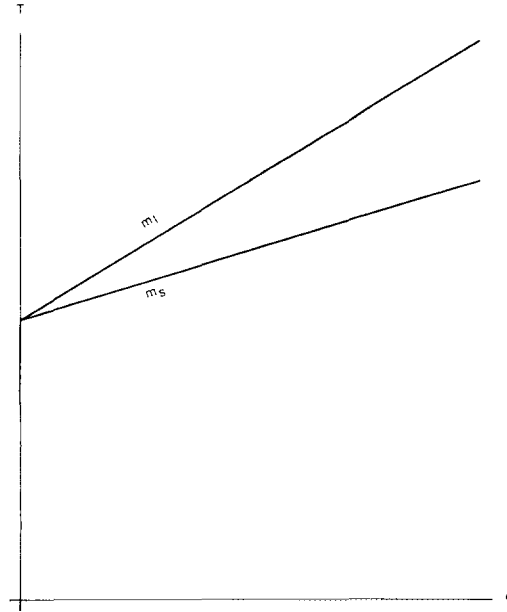


FIG. 3. The linear approximation to the ideal solution phase diagram for small concentration. The liquidus and solidus curves are approximated by line segments of slope m_l , m_s , respectively. This approximation is the basis of the simple sharp-interface models for phase interface dynamics in alloys.

The Phase Diagram

The algebraic system of equations

$$\ln \frac{1-c^+}{1-c^-} = a, \quad \ln \frac{c^+}{1-c^+} - \ln \frac{c^-}{1-c^-} = b \quad (6.19a), (6.19b)$$

has a unique solution,

$$c^- = \frac{1-e^{-a}}{1-e^{-b}}, \quad c^+ = \frac{1-e^a}{1-e^{-b}}, \quad (6.20)$$

so that $c^+/c^- = e^{a+b}$. Equations (6.14), (6.18) correspond to (6.19a), (6.19b) with

$$a := \frac{[s_2]_{\text{eq}}}{R} \left(1 - \frac{T_2}{T} \right), \quad b := -\frac{2N(T)}{RT},$$

so that the solidus $c^-(T)$ and liquidus $c^+(T)$ are determined as

$$c^-(T) = \frac{1 - e^{-([s_2]_{\text{eq}}/R)(1 - T_2/T)}}{1 - e^{-2N(T)/(RT)}}, \quad c^+(T) = \frac{1 - e^{([s_2]_{\text{eq}}/R)(1 - T_2/T)}}{1 - e^{2N(T)/(RT)}}. \quad (6.21)$$

Hence, the phase diagram is completely determined by (6.21) in terms of the two melting temperatures T_1 , T_2 and the jumps in entropy density $[s_1]_{\text{eq}}$, $[s_2]_{\text{eq}}$. In particular, the behavior for temperatures T near T_2 can be approximated easily by expanding (6.20) in a Taylor sense for small a (but fixed b) with the result:

$$c^- \simeq m_s^{-1}(T - T_2), \quad c^+ \simeq m_l^{-1}(T - T_2), \quad |1 - T_2/T| \ll 1 \quad (6.22)$$

$$m_s := -\frac{RT_2}{[s_2]_{\text{eq}}}(1 - e^{-2N/RT_2}), \quad m_l := -\frac{RT_2}{[s_2]_{\text{eq}}}(1 - e^{2N/RT_2}). \quad (6.23)$$

This determines the slopes of the solidus and liquidus curves (Fig. 3) as m_s and m_l , respectively, with the ratio $m_l/m_s = e^{2N/RT_2}$. Due to the symmetry, the solidus slope near T_1 is m_l while the liquidus slope is m_s .

Thus, the melting temperatures T_1 and T_2 establish a ‘‘baseline’’ in the phase diagram (Fig. 2) while $2N/RT$ determines the magnitude of spreading between the liquidus and solidus curves through $2N/RT_2 = \log(m_l/m_s)$. If we write $N(T)$ in the form

$$\begin{aligned} 2N(T) = & \langle [s_i]_{\text{eq}} \rangle_{1,2} (T_1 - T_2) + ([s_2]_{\text{eq}} - \langle [s_i]_{\text{eq}} \rangle_{1,2})(T - T_2) \\ & + ([s_1]_{\text{eq}} - \langle [s_i]_{\text{eq}} \rangle_{1,2})(T - T_1) \end{aligned} \quad (6.24)$$

with $\langle [s_i]_{\text{eq}} \rangle_{1,2} := \frac{1}{2}([s_1]_{\text{eq}} + [s_2]_{\text{eq}})$ then it is clear that the spreading is a measure of the entropy difference between two phases. In the limit $[s_i]_{\text{eq}}/R \rightarrow 0$, one has from (6.21)

$$c^\pm(T) \simeq \frac{[s_2]_{\text{eq}}}{2N(T)}(T - T_2) \quad (6.25)$$

$$c^\pm(T) \simeq \frac{T - T_2}{T_1 - T_2} \quad \text{if } [s_1]_{\text{eq}} = [s_2]_{\text{eq}}. \quad (6.26)$$

Consequently, $c^+(T)$ and $c^-(T)$ both converge to the straight line between T_1 and T_2 if $[s_1]_{\text{eq}}$ and $[s_2]_{\text{eq}}$ are equal and approach zero. If these jumps in entropy are not equal then the liquidus and solidus curves converge to a curve which deviates from this straight line by an amount which is of order $([s_i]_{\text{eq}} - \langle [s_i]_{\text{eq}} \rangle_{1,2})$.

The emergence of $[s_i]_{\text{eq}}/R$ as the dimensionless constants which determine the separation between liquidus and solidus curves in the phase diagram can be examined as follows. The melting temperatures, T_1 , T_2 , determine the baseline slope, while $\langle [s_i]_{\text{eq}} \rangle_{1,2}/R$ determines the unique pair of curves $c^-(T)$, $c^+(T)$ given by

$$c_{\text{sym}}^\pm(T) = \frac{1 - \exp\{\pm(\langle [s_i]_{\text{eq}} \rangle_{1,2}/RT)(T - T_2)\}}{1 - \exp\{\pm(\langle [s_i]_{\text{eq}} \rangle_{1,2}/RT)(T_1 - T_2)\}} \quad (6.27)$$

which have a particular symmetry about the baseline (6.26). If $[s_1]_{\text{eq}} = [s_2]_{\text{eq}} = \langle [s_i]_{\text{eq}} \rangle_{1,2}$ then the liquidus and solidus are given by c_{sym}^\pm . Otherwise, the

difference in the entropy jump ($\langle [s_i]_{\text{eq}} \rangle_{1,2} - [s_i]_{\text{eq}}$) results in a distortion of c_{sym}^{\pm} to the curves c^{\pm} given by (6.21).

The origin of the dimensionless parameters $[s_i]/R$ can be most easily understood for the symmetric case $[s_1]_{\text{eq}} = [s_2]_{\text{eq}} = \langle [s_i]_{\text{eq}} \rangle_{1,2} = [s]_{\text{eq}}$. The term $[s]_{\text{eq}}/R$ is clearly a comparison of two distinct sources of entropy in the equations (6.3)–(6.5). The term $[s]_{\text{eq}}$ arises from the entropy contribution to the free energy which results in the term $\varepsilon([s]_{\text{eq}}/3\sigma)\{T - T_1c - T_2(1-c)\}$ that is a measure of the free energy shift due to the change in phase. (Note that the origin of this term in the free energy is a term in which this is multiplied by the order parameter. The same term is, of course, in (6.5), this time differentiated with respect to concentration.) The scale R arises exclusively from the entropy of mixing term $RT\{c \ln c + (1-c) \ln(1-c)\}$. Consequently, the dimensionless number $[s]_{\text{eq}}/R$ is a measure of the entropy of phase change compared to the entropy of mixing. The latter is, of course, completely independent of phase. As $[s]_{\text{eq}}/R$ is made larger, the jump in concentrations is larger since the liquidus and solidus are further apart (Fig. 2).

The Concentration Profile

The transition layer in ψ is a consequence of the basic equation (6.10). The transition layer in c occurs as a result of (6.12) and the transition layer in ψ . The role of ψ in (6.12) and, equivalently, in (6.5) is to force a transition layer on c between phases and then to vanish in the pure phases, thereby allowing (6.5) to describe mixing in pure phases as discussed in the next section.

One of the subtleties in the development of the transition layer is the introduction of the temperature through an integration constant in the ordinary differential equation (6.12). In particular, it is clear that if A is a fixed constant, independent of temperature, then the magnitude of the transition in c will depend on temperature only through the RT term and will not vanish as $T \rightarrow T_1$ or $T \rightarrow T_2$. In fact, the integration constant A is a boundary condition for the first-order ordinary differential equation (6.12). Then, a mathematical requirement for a unique solution is the specification of the value of \hat{c}^0 at one point, e.g., $+\infty$ or $-\infty$. This means that the solution \hat{c}^0 to (6.12) which has the general form

$$\hat{c}^0 = \frac{e^{A/RT} e^{-N/RT\hat{\psi}^0}}{1 + e^{A/RT} e^{-N/RT\hat{\psi}^0}} \quad (6.28)$$

is completely determined once the boundary value is specified. In terms of the phase diagram, the specification of the boundary condition at $-\infty$ means (with our convention of taking the solid on the left) that the concentration on the solidus is fixed for that particular value of T which appears in (6.12). Of course, the value of \hat{c}^0 is then determined by (6.28) so that the two points $c^+(T)$ and $c^-(T)$ are both determined by A . Thus in principle, one could use a phase diagram to evaluate A .

Throughout this part of the analysis, the temperature has been treated as a constant due to equilibrium conditions. In the next section, we will see that the inner expansion for the temperature in the *dynamic* situation will be constant to leading order;

consequently, the temperature can be treated as a constant for interface conditions even in the dynamics. This is equivalent to the statement that T is continuous across the interface. These conditions will be supplemented by two other conditions relating to energy and mass balance at the interface.

The Non-ideal Case

We now consider the non-ideal situation, namely $\Omega = \Omega_0 + \Omega_1 T \neq 0$. The equilibrium concentration equation is

$$0 = \nabla \left\{ N\psi + RT \ln \frac{c}{1-c} + \Omega(T)(1-2c) \right\} \quad (6.29)$$

so that the analysis which leads to (6.14) now yields

$$-\frac{2N}{RT} = \left[\ln \frac{c}{1-c} - 2 \frac{\Omega}{RT} c \right]^+. \quad (6.30)$$

The relation (6.18) is generalized to

$$1 - \frac{T_2}{T} = \frac{R}{[s_2]_{\text{eq}}} \ln \frac{1-c^+}{1-c^-} + \frac{\Omega}{2[s_2]_{\text{eq}}} (c^{+2} - c^{-2}). \quad (6.31)$$

Equations (6.30) and (6.31) are again a coupled algebraic system for $c^+(T)$ and $c^-(T)$, whose solutions are the liquidus and solidus lines in the phase diagram; however, a closed form solution for $c^\pm(T)$ is no longer possible. In the small c approximation the solution to (6.30) and (6.31) agrees with those of (6.14) and (6.18).

7. COMPLETE ASYMPTOTIC ANALYSIS OF PHASE FIELD ALLOY MODEL

We now construct an asymptotic solution for the complete model in a dynamical setting. We assume all parameters are fixed except for ε which is asymptotically small, compared to other length scales, e.g., length of domain. As in the pure model, it is a consequence of the analysis that the interface thickness is of order ε . The interface Γ is defined as the set of points in Ω at which $\psi = 0$. Letting $x := (x_1, x_2)$ we define $r(x, t; \varepsilon)$ within a sufficiently small neighborhood of Γ as the signed distance from x to Γ , with the convention that $+$ is the direction of positive ψ and $-$ is the direction of negative ψ . We suppose that r is a smooth function in a neighborhood of Γ . The interface is described by the equation

$$r(x, t; \varepsilon) = 0 \quad (7.1)$$

and r has the properties

$$|\nabla r| = 1 \quad \text{and} \quad \Delta r = \kappa \quad (7.2)$$

on the interface Γ , with κ as the curvature.

The second coordinate, s , is defined as the arclength from a fixed point on the interface (depending smoothly on t), so that (r, s) forms a local orthogonal coordinate system. An inner variable $z := r/\varepsilon$ is defined by stretching the normal coordinate. The outer and inner expansions of the concentration, temperature, and phase are obtained by writing these terms in a finite power series in ε , where the coefficients may depend on the space and time variables, but not on ε . One has for any integer L , the outer expansion

$$\begin{aligned} c(r, s, t; \varepsilon) &\simeq c^0(r, s, t) + \varepsilon c^1(r, st) + \cdots + \varepsilon^L c^L(r, s, t) \\ T(r, s, t; \varepsilon) &\simeq T^0(r, s, t) + \varepsilon T^1(r, st) + \cdots + \varepsilon^L T^L(r, s, t) \\ \psi(r, s, t; \varepsilon) &\simeq \psi^0(r, s, t) + \varepsilon \psi^1(r, st) + \cdots + \varepsilon^L \psi^L(r, s, t), \end{aligned} \quad (7.3)$$

where the sum of the first L terms are intended as an approximation of the form $|c - (c^0 + \varepsilon c^1 + \cdots + \varepsilon^L c^L)| \leq A\varepsilon^{L+1}$ for some A independent of ε . The terms on the right may be discontinuous, and we use $f|_{r_{\pm}}$ or f_{\pm} to denote the limiting values of f as approached from the side where $r > 0$ or $r < 0$, respectively.

By writing c, T, ψ in terms of the inner variable, $z = r/\varepsilon$, with $\hat{c}(z, s, t; \varepsilon) = c(r, s, t; \varepsilon)$, one can write in a similar way

$$\begin{aligned} \hat{c}(z, s, t; \varepsilon) &\simeq \hat{c}^0(z, s, t) + \varepsilon \hat{c}^1(z, st) + \cdots + \varepsilon^L \hat{c}^L(z, s, t) \\ \hat{T}(z, s, t; \varepsilon) &\simeq \hat{T}^0(z, s, t) + \varepsilon \hat{T}^1(z, st) + \cdots + \varepsilon^L \hat{T}^L(z, s, t) \\ \hat{\psi}(z, s, t; \varepsilon) &\simeq \hat{\psi}^0(z, s, t) + \varepsilon \hat{\psi}^1(z, st) + \cdots + \varepsilon^L \hat{\psi}^L(z, s, t). \end{aligned} \quad (7.4)$$

Note that $\hat{\psi}(0, s, t; \varepsilon) = 0$ by definition.

For the pure phase field model, which involves only ψ and T , transition layers occur in ψ and $\nabla T \cdot n$. For the alloy, transition layers will occur in ψ and c , as indicated by the discussion of equilibrium and again in $\nabla T \cdot n$ if the interface is moving.

The inner expansion is expected to approximate the behavior of the functions near the interface while the outer expansion is to be valid far (on a scale of ε) from the interface. Since the terms in the outer expansion or their derivatives may be discontinuous, boundary conditions on the interface must be provided by the matching conditions of asymptotic analysis which provide a connection between the two approximations. For our purposes, the two conditions

$$\begin{aligned} \lim_{r \rightarrow 0_{\pm}} c^0(r, s, t) &= \lim_{z \rightarrow \pm\infty} \hat{c}^0(z, s, t), \\ \lim_{r \rightarrow 0_{\pm}} c_r^0(r, s, t) &= \lim_{z \rightarrow \pm\infty} c_z^1(r, s, t) \end{aligned} \quad (7.5)$$

will suffice.

For convenience we make the following definitions:

$$\begin{aligned}
 E(T, c) &:= [s_2]_{\text{eq}} (T - T_2) - c [[s_i]_{\text{eq}} (T - T_i)]_{1,2} =: E_1 + E_2 c \\
 H(c) &:= \frac{[s_2]_{\text{eq}}}{2} T_2 - \frac{c}{2} [[s_i]_{\text{eq}} T_i]_{1,2} =: H_1 + H_2 c \\
 M(\psi, c) &:= M_1(c) + M_2(\psi) \\
 M_1(c) &:= \Omega_0(1 - 2c) \\
 M_2(\psi, c) &:= [C_v T_i - \bar{g}_i]_{1,2} - [[s_i]_{\text{eq}} T_i]_{1,2} - \frac{\psi}{2} [[s_i]_{\text{eq}} T_i]_{1,2} \\
 G(T, \psi, c) &:= G_1(T, \psi, c) + G_2(T) \\
 G_1(T, \psi, c) &:= N(T) \psi + RT \ln \frac{c}{1-c} + C_v T \ln T_1/T_2 + \Omega(T)(1 - 2c) \\
 G_2(T) &:= \frac{T}{2} [\langle s_i \rangle_{\text{eq}}]_{1,2} \\
 N(T) &:= \frac{1}{2} [[s_i]_{\text{eq}} (T - T_i)]_{1,2}, \quad \tilde{D} := RTD.
 \end{aligned} \tag{7.6}$$

Equations (6.3)–(6.5) can be written as

$$q(T) \varepsilon^2 \psi_t = \varepsilon^2 \Delta \psi + \frac{1}{2} (\psi - \psi^3) + \frac{\varepsilon}{3\sigma(T)} E(T, c) \tag{7.7}$$

$$C_v T_i + H(c) \psi_t + M(\psi, c) c_t = \nabla \cdot k \nabla T \tag{7.8}$$

$$c_t = \nabla \cdot Dc(1 - c) \nabla G(T, \psi, c). \tag{7.9}$$

The transformation $(x_1, x_2, t) \rightarrow (r, s, t)$ yields for an arbitrary f

$$\Delta f \rightarrow f_{rr} + \Delta r f_r + |\nabla s|^2 f_{ss} + \Delta s f_s, \quad f_t \rightarrow f_t + r_t f_r + s_t f_s. \tag{7.10}$$

In terms of the new variables, Eqs. (6.3)–(6.5) have the form

$$q(T)(\psi_t + \psi_r r_s + \psi_s s_t) = \varepsilon^2 (\psi_{rr} + |\nabla s|^2 \psi_{ss} + \Delta r \psi_r + \Delta s \psi_s) + \frac{1}{2} (\psi - \psi^3) + \frac{\varepsilon}{3\sigma} E(T, c) \tag{7.11}$$

$$C_v (T_t + r_t T_r + s_t T_s) + H(c) \psi_t + M(\psi, c) c_t = \nabla \cdot k \nabla T \tag{7.12}$$

$$c_t + r_t c_r + s_t c_s = D(\psi) c(1 - c) \Delta G + \nabla(G(\psi) c(1 - c)) \cdot \nabla G. \tag{7.13}$$

The main result of this section is summarized below:

PROPOSITION 7.1. *In the limit $\varepsilon \rightarrow 0$ with all other parameters held fixed, there exists a formal asymptotic solution (ψ, T, c) of the phase field alloy model (6.3)–(6.5)*

which is governed by the following sharp interface model (with + for liquid and – for solid),

$$\begin{aligned} C_v T_t + ([C_v T_i - \bar{g}_i]_{1,2} - (1 \pm \frac{1}{2})[[s_i]_{\text{eq}} T_i]_{1,2} - 2\Omega_0 c + \Omega_0) c_t \\ = \nabla \cdot k \nabla T \end{aligned} \quad (7.14)$$

$$\begin{aligned} c_t = \nabla \cdot \tilde{D} \nabla c - 2\nabla \cdot \frac{\tilde{D}}{RT} c(1-c) \Omega(T) \nabla c + \nabla \cdot \frac{\tilde{D}}{T} c(1-c) \\ \times \left\{ \ln \frac{c}{1-c} + \frac{\Omega_1}{R} (1-2c) + \frac{C_v}{R} (nT_1/T_2 \pm [[s_i]_{\text{eq}}]_{1,2}) \right\} \nabla T \end{aligned} \quad (7.15)$$

$$[T]_{\pm}^+ = 0 \quad (7.16)$$

$$\begin{aligned} -k[\nabla T \cdot n]^+ = \left\{ [s_2]_{\text{eq}} T_2 - [[s_i]_{\text{eq}} T_i]_{1,2} \left(\frac{c_+ + c_-}{2} + [c]_{\pm}^+ \right) \right. \\ \left. + [C_v T_i - \bar{g}_i]_{1,2} [c]_{\pm}^+ + \Omega_0([c]_{\pm}^+ + [c^2]_{\pm}^+) \right\} v \end{aligned} \quad (7.17)$$

$$-\frac{2N}{RT} = \left[\ln \frac{c}{1-c} - 2 \frac{\Omega(T)}{RT} c \right]^+ \quad (7.18)$$

$$\begin{aligned} -v[c]_{\pm}^+ = [\tilde{D} \nabla c \cdot n]_{\pm}^+ - 2\Omega(T) \left[\frac{\tilde{D}}{RT} c(1-c) \nabla c \cdot n \right]_{\pm}^+ \\ + \left[\frac{\tilde{D}}{RT} c(1-c) \left\{ \frac{1}{2} [\langle s_i \rangle_{\text{eq}} \pm [s_i]_{\text{eq}}]_{1,2} \right. \right. \\ \left. \left. + R \ln \frac{c}{1-c} + \Omega_1(1-2c) \right\} \nabla T \cdot n \right]_{\pm}^+ \end{aligned} \quad (7.19)$$

$$- \{q(T)v + \kappa\} \sigma(T) = [s_2]_{\text{eq}} (T - T_2) - RT \ln \frac{1-c_+}{1-c_-} - \Omega(T)[c^2]_{\pm}^+, \quad (7.20)$$

where Eqs. (7.14) and (7.15) are valid in $\Omega \setminus \Gamma(t)$ and (7.16)–(7.20) are valid on the interface $\Gamma(t)$. The parameters \bar{g}_i , Ω_0 , Ω_1 , Ω , N , \tilde{D} , $q(T)$, $\sigma(T)$ are defined by (3.26), (6.11), (7.6), (7.7), and (6.1).

Verification of Proposition 7.1. The successive orders in the outer expansion are obtained by formally equating powers of ε in (7.7)–(7.9) or (7.11)–(7.13).

The outer expansion $O(1)$. Equation (7.7) implies that

$$\psi^0 - \psi^{03} = 0 \quad \text{or} \quad \psi^0 = \pm 1. \quad (7.21)$$

Note that we do not make use of the solution $\psi^0 = 0$ which is not stable in the dynamical systems sense. By utilizing the solution (7.21) one observes that the $O(1)$ expansions for Eqs. (7.7) and (7.8) are

$$C_v T_t^0 + M^0(\pm 1, c^0) c_t^0 = \nabla \cdot k \nabla T^0 \quad (7.22)$$

$$c_t^0 = \nabla \cdot D c^0 (1 - c^0) \nabla G^0(T^0, \pm 1, c^0) \quad (7.23)$$

which are identical to the pure phase equations (7.14) and (7.15).

The inner expansion. To derive the interface relations, we focus on the inner expansion, which is obtained by rewriting (7.11)–(7.13) in terms of the inner variable $z := r/\varepsilon$:

$$\begin{aligned} \hat{\psi}_{zz} + \frac{1}{2}(\hat{\psi} - \hat{\psi}^3) + \varepsilon \left\{ \frac{E}{3\sigma}(\hat{T}, \hat{c}) - q(\hat{T}) r_t \hat{\psi}_z + \Delta r \hat{\psi}_z \right\} \\ + \varepsilon^2 \{ |\nabla s| \hat{\psi}_{ss} + \Delta s \hat{\psi}_s - q(\hat{T}) \hat{\psi}_t - q(\hat{T}) s_t \hat{\psi}_s \} = 0 \end{aligned} \quad (7.24)$$

$$\begin{aligned} k \hat{T}_{zz} + \varepsilon \{ k \Delta r \hat{T}_z - C_v r_t \hat{T}_z - H(\hat{c}) r_t \hat{\psi}_z - M(\hat{\psi}, \hat{c}) r_t \hat{c}_z \} \\ + \varepsilon^2 \{ k |\nabla s|^2 \hat{T}_{ss} + k \Delta s \hat{T}_s - C_v \hat{T}_t - s_t \hat{T}_s - H(\hat{c}) \hat{\psi}_t - H(\hat{c}) s_t \hat{\psi}_s \} = 0 \end{aligned} \quad (7.25)$$

$$\begin{aligned} (D(\hat{\psi}) \hat{c}(1 - \hat{c}) G_z)_z + \varepsilon \{ -r_t \hat{c}_z + \Delta r G_z \} \\ + \varepsilon^2 \{ -\hat{c}_t - s_t \hat{c}_s + |\nabla s|^2 G_{ss} + \Delta s G_s + |\nabla s|^2 (D(\hat{\psi}) \hat{c}(1 - \hat{c}) G_s) \} = 0. \end{aligned} \quad (7.26)$$

The inner expansion $O(1)$. The inner expansions are then obtained by formally equating powers of ε in (7.24)–(7.26). The $O(1)$ terms are

$$\hat{\psi}_{zz} + \frac{1}{2}[\hat{\psi}^0 - (\hat{\psi}^0)^3] = 0, \quad (7.27)$$

$$\hat{T}_{zz} = 0, \quad (7.28)$$

$$(D(\hat{\psi}^0) \hat{c}^0(1 - \hat{c}^0) G_z)_z = 0. \quad (7.29)$$

With our convention that positive r is liquid, the solution to (7.27) is

$$\hat{\psi}_z^0 = \tanh z/2. \quad (7.30)$$

The general solution to (7.28) is a linear function, however, as we seek to construct solutions subject to the bound $0 \leq c^0 \leq 1$, we have the temperature to leading order as

$$\hat{T}^0(z, s, t) = a_1(s, t), \quad (7.31)$$

where a_1 is independent of z , but it may depend on s and t . Similarly, the boundedness requirement on \hat{c} also implies that the constant of the first integration must vanish, so that

$$G_z = 0 \quad \text{or} \quad G(\hat{T}^0, \hat{\psi}^0, \hat{c}^0) = a_2, \quad (7.32)$$

where $a_2(s, t)$ is independent of z . Note, however, that a_2 may depend on $\hat{T}^0 = a_1$, as discussed in Section 6 for the equilibrium problem.

The interface condition (7.18) can now be obtained as an immediate consequence of (7.32) which implies that

$$\lim_{z \rightarrow -\infty} G(\hat{T}^0, \hat{\psi}^0, \hat{c}^0) - \lim_{z \rightarrow \infty} (\hat{T}^0, \hat{\psi}^0, \hat{c}^0) = 0 \quad (7.33)$$

or

$$2N(\hat{T}^0) + R\hat{T}^0 \left[\ln \frac{\hat{c}^0}{1 - \hat{c}^0} \right]_{z=-\infty}^{z=+\infty} - 2\Omega(\hat{T}^0)[c]_{z=-\infty}^{z=+\infty} = 0. \quad (7.34)$$

Upon application of the first of the matching conditions (7.5), one obtains

$$2N(T^0) + RT^0 \left[\ln \frac{c^0}{1 - c^0} \right]_{-}^{+} - 2\Omega(r^0)[c]_{-}^{+} = 0. \quad (7.35)$$

The interface condition (7.16), which expresses the continuity of the temperature, follows from (7.31) and (7.5). The other interface conditions, namely (7.17), (7.19), and (7.20) are obtained from the $O(\varepsilon)$ analysis.

The inner expansion $O(\varepsilon)$. Formally equating the first powers of ε in (7.24), (7.25), and (7.26) one has

$$\hat{\psi}_{zz}^1 + \frac{1}{2}(1 - 3(\hat{\psi}^0)^2)\hat{\psi}^1 = q(T)r_i^0\hat{\psi}_z^0 - \Delta r^0\hat{\psi}_z^0 - \frac{E(\hat{T}^0)}{3\sigma(\hat{T}^0)} \quad (7.36)$$

$$kT_{zz}^1 - H(\hat{c}^0)r_i^0\hat{\psi}_z^0 - M(\hat{\psi}^0, \hat{c}^0)r_i^0\hat{c}_z^0 = 0 \quad (7.37)$$

$$(D(\hat{\psi}^0)\hat{c}^0(1 - \hat{c}^0)G_z^1)_z - r_i^0\hat{c}_z^0 = 0, \quad (7.38)$$

where (7.32) has been used in the last equation and G^1 is defined by $G = G^0 + \varepsilon G^1$. In order to evaluate G_z^1 , we write

$$G(\hat{T}, \hat{\psi}, \hat{c}) = G(\hat{T}^0, \hat{\psi}^0, \hat{c}^0) + \varepsilon \hat{T}^1 D_1 G(\hat{T}^0, \hat{\psi}^0, \hat{c}^0) \\ + \varepsilon \hat{\psi}^1 D_2(\hat{T}^0, \hat{\psi}^0, \hat{c}^0) + \varepsilon \hat{c}^1 D_3 G(\hat{T}^0, \hat{\psi}^0, \hat{c}^0), \quad (7.39)$$

where D_i denotes differentiation with respect to the i th entry of G . Then G_z^1 , which is the $O(\varepsilon)$ term in (7.39), is given by

$$G_z^1 = \frac{\hat{\psi}_z^0}{2} [[s_i]_{\text{eq}}(\hat{T}^1 - T_i)]_{1,2} + \frac{\hat{\psi}^0}{2} [[s_i]_{\text{eq}}]_{1,2} \hat{T}_z^1 \\ + \frac{\hat{T}_z^1}{2} [[s_i]_{\text{eq}}]_{1,2} + R\hat{T}_z^1 \ln \frac{\hat{c}^0}{1 - \hat{c}^0} + R\hat{T}^1 \frac{\hat{c}_z^0}{\hat{c}^0(1 - \hat{c}^0)} \\ + C_v \hat{T}_z^1 \ln(T_1/T_2) + \Omega_1 \hat{T}_z^1 (1 - 2\hat{c}^0) - 2\Omega_1 \hat{T}^1 \hat{c}_z^0 \\ + \frac{\hat{\psi}_z^1}{2} [[s_i]_{\text{eq}}(\hat{T}^0 - T_i)]_{1,2} + R\hat{T}^0 \left(\frac{\hat{c}^1}{\hat{c}^0(1 - \hat{c}^0)} \right)_z - 2\Omega(\hat{T}^0)\hat{c}_z^1. \quad (7.40)$$

We analyze (7.38) by integrating with respect to z , yielding

$$D(\hat{\psi}^0) \hat{c}^0(1 - \hat{c}^0) G_z^1 = r_i^0 \hat{c}_z^0 + a_3(s, t). \quad (7.41)$$

One has $T_z^0 = 0$ (by (7.31)) and $\lim_{z \rightarrow \pm\infty} \hat{\psi}_z^0 = 0$ (by (7.30)) so that (7.32), together with (7.6) implies that $\lim_{z \rightarrow \pm\infty} \hat{c}_z^0 = 0$.

By subtracting the $\lim_{z \rightarrow -\infty}$ of (7.41) from $\lim_{z \rightarrow +\infty}$, using (7.40), and recovering the original (outer) variables by means of the matching conditions (7.5), one obtains the interface condition (7.19) as the following leading order relation, i.e.,

$$\left[D(\psi^0) c^0(1 - c^0) \left\{ \frac{1}{2} [[s_i]_{\text{eq}} + \psi^0 [s_i]_{\text{eq}}]_{1,2} + R \ln \frac{c^0}{1 - c^0} + \Omega_1(1 - 2c^0) \right\} T_r^0 + D(\psi^0) \{ -2\Omega(T^0) c^0(1 - c^0) + RT^0 \} c_r^0 \right]_{-}^{+} = -v [c^0]_{-}^{+}. \quad (7.42)$$

Note that $D(\psi^0)$ is just $D(1)$ if $r > 0$, i.e., the diffusion coefficient in the liquid phase, and analogously for the solid. This condition, which leads to (7.19), is a generalization of the simplest conservation of mass condition which would be given by the right-hand side of (7.42) and the last term on the left-hand side.

To obtain the next interface condition, namely (7.17), we apply a similar procedure to (7.37), which we rewrite as

$$k \hat{T}_{zz}^1 - \frac{[s_2]_{\text{eq}}}{2} T_2 r_i^0 \hat{\psi}_z^0 - ([C_v T_i - \bar{g}_i]_{1,2} - [[s_i]_{\text{eq}} T_i]_{1,2} + \Omega_0) r_i^0 \hat{c}_z^0 - 2\Omega_0 \hat{c}^0 \hat{c}_z^0 r_i^0 - \frac{[[s_i]_{\text{eq}} T_i]_{1,2}}{2} r_i^0 (\hat{c}^0 \hat{\psi}^0)_z = 0. \quad (7.43)$$

By writing $2\hat{c}^0 \hat{c}_z^0$ as $(\hat{c}^{0^2})_z$, we integrate (7.43) to obtain

$$k \hat{T}_z^1 - \frac{[s_2]_{\text{eq}}}{2} T_2 r_i^0 \hat{\psi}^0 - ([C_v T_i - \bar{g}_i]_{1,2} - [[s_i]_{\text{eq}} T_i]_{1,2} + \Omega_0) r_i^0 \hat{c}^0 - \Omega_0 r_i^0 (\hat{c}^0)^2 - \frac{1}{2} [[s_i]_{\text{eq}} T_i]_{1,2} r_i^0 \hat{c}^0 \hat{\psi}^0 = a_4(s, t). \quad (7.44)$$

Taking $\lim_{z \rightarrow -\infty}$ of (7.44), subtracting it from the $\lim_{z \rightarrow +\infty}$ and, using the matching conditions (7.5) one has the generalized latent heat condition

$$-k [T_r^0]_{r_{\pm}} = \left\{ [s_2]_{\text{eq}} T_2 - [[s_i]_{\text{eq}} T_i]_{1,2} \left(\frac{c^{0^+} + c^{0^-}}{2} + [c^0]_{-}^{+} \right) + [C_v T_i - \bar{g}_i]_{1,2} [c^0]_{-}^{+} + \Omega_0 ([c^0]_{-}^{+} + [c^{0^2}]_{-}^{+}) \right\} v. \quad (7.45)$$

Finally, the phase equation (7.36) has $\hat{\psi}_z^0$ (given by (7.30)) as its homogeneous solution, i.e.,

$$\mathcal{L}\hat{\psi}_z^0 := (\hat{\psi}_z^0)_{zz} + \frac{1}{2}(1 - 3(\hat{\psi}^0)^2)\hat{\psi}_z^0 = 0, \quad (7.46)$$

and $\hat{\psi}_z^0$ is a simple eigenfunction corresponding to the zero eigenvalue of the linear operator \mathcal{L} . The Fredholm alternative theorem then implies that a necessary and sufficient condition for the solvability of (7.36) is the orthogonality of $\hat{\psi}_z^0$ with the right-hand side of (7.36), i.e.,

$$\int_{-\infty}^{\infty} \hat{\psi}_z^0 \left\{ (vq(\hat{T}^0) + \kappa)\hat{\psi}_z^0 + \frac{E(\hat{T}^0, \hat{c}^0)}{3\sigma(\hat{T}^0)} \right\} dz = 0, \quad (7.47)$$

where we have used (7.2) and $-r_l^0 = v$. Note that the necessity of (7.47) in this case is easily obtained by (i) multiplying (7.46) by $\hat{\psi}_z^0$ and (7.36) by $\hat{\psi}_z^0$, (ii) subtracting one from the other, (iii) integrating from $z = -\infty$ to $z = \infty$, and (iv) using integration by parts along with the boundary values $\hat{\psi}_z^0(\pm\infty) = 0$.

Since v , κ , and \hat{T}^0 are all independent of z , the first integral in (7.47) is evaluated by computing $\int_{-\infty}^{\infty} (\hat{\psi}_z^0)^2 dz = \frac{2}{3}$. To evaluate the second integral, we first need to compute $\int_{-\infty}^{\infty} \hat{\psi}_z^0 \hat{c}^0 dz$. To do this, we use (7.32) which we write as

$$\hat{\psi}_z^0 = -\frac{R\hat{T}^0}{N} \frac{\hat{c}_z^0}{\hat{c}^0(1-\hat{c}^0)} + 2 \frac{\Omega(\hat{T}^0)}{N} \hat{c}_z^0. \quad (7.48)$$

Using this expression we now evaluate the integral as

$$\begin{aligned} \int_{-\infty}^{\infty} \hat{\psi}_z^0 \hat{c}^0 dz &= \int_{-\infty}^{\infty} \hat{c}^0 \left\{ -\frac{R\hat{T}^0}{N} \frac{\hat{c}_z^0}{\hat{c}^0(1-\hat{c}^0)} + \frac{2\Omega}{N} \hat{c}_z^0 \right\} dz \\ &= \frac{R\hat{T}^0}{N} [\ln(1-\hat{c}^0)]_{-\infty}^{\infty} + \frac{\Omega}{N} [\hat{c}^{0^2}]_{-\infty}^{\infty}. \end{aligned} \quad (7.49)$$

Substituting (7.49) in (7.47) and using the matching conditions (7.5) for \hat{c}^0 and \hat{T}^0 to return to the original (outer) variables, we obtain finally the relation

$$\{-q(T^0)v - \kappa\} \sigma(T^0) = [s_2]_{\text{eq}}(T - T_2) - RT \ln \frac{1 - c^{0+}}{1 - c^{0-}} - \Omega \{(c^{0+})^2 - (c^{0-})^2\}. \quad (7.50)$$

Hence, relation (7.20), which is a generalization of the Gibbs–Thomson relation, $-\sigma\kappa = [s_2]_{\text{eq}}(T - T_2)$, is thereby derived. ■

Discussion of Proposition 7.1. We have shown that our phase-alloy equations lead to a system of differential equations with a set of interface conditions, namely (7.14)–(7.20). Both the phase-alloy system and the sharp interface system thus incorporate in a consistent way the thermodynamical and kinetic principles

involved in a moving phase boundary involving a mixture. While the phase-alloy model can be expected to remain valid for complex geometries of the interface such as self-intersections, the sharp interface model above is well defined only for smooth interfaces.

An interesting question is the extent to which the concentration on the two sides of the interface c_+ and c_- differ from their values in equilibrium, i.e., the liquidus $c_+(T)$ and solidus $c_-(T)$. Since T is continuous across the interface, a given value of T determines $c_+(T)$ and $c_-(T)$ via (7.18) and (7.20). Since the liquidus and solidus (in equilibrium) are determined by (7.18) and (7.20) with time derivatives set at 0, the dynamic values of $c_+(T)$ and $c_-(T)$ differ from the equilibrium only through the left-hand side of (7.20). Note that for the pure material, 2, the planar equilibrium “phase diagram” is the trivial $T = T_2$, which is modified in non-equilibrium by adding the surface tension and velocity terms, i.e.,

$$T = T_2 - \frac{\sigma(T)}{[s_2]_{\text{eq}}} (\kappa + q(T)). \tag{7.51}$$

Although the system (7.18), (7.20) is more complex than (7.51), the result is analogous in that the equilibrium phase diagram (i.e., (7.20), with the left-hand side set equal to 0, and (7.18)) is perturbed by adding the same velocity and curvature terms to the pure melting temperature.

The simpler models. We consider simplifications of both sets of equations (sharp and diffuse) to illustrate how the traditional (simpler) sharp interface models arise as we remove progressively the following levels of physics from our models:

(I) Assume the entropy densities s_i , are identical for both materials in each phase so that

$$[\langle s_i \rangle_{\text{eq}} \pm [s_i]_{\text{eq}}]_{1,2} = 0, \quad [s_i]_{\text{eq}} \neq 0, \quad T_1 \neq T_2.$$

(IIa) Assume that the leading correction G_E to the ideal solution in (3.25) has constant coefficient, $\Omega(T) = \Omega_0$ (i.e., $\Omega_1 := 0$).

(IIb) Assume that the free energy, g , in (3.27) is ideal so that $\Omega(T) = \Omega_0 = \Omega_1 = 0$.

(III) (Small c approximation). Linearize in c and its derivatives and in the derivatives of T . The use of a small c approximation is compatible with a small gradient T since T is near T_2 in the phase diagram (Fig. 2) when c is small. Hence, while T will not be small, one can expect that $\nabla T \cdot n$ and T_t will be small.

The physical approximations (I)–(III) lead to the following two results which are corollaries of Proposition 7.1.

PROPOSITION 7.2. *In the limit $\varepsilon \rightarrow 0$ with all other parameters held fixed, the reduced phase field alloy equations obtained from (6.3)–(6.5) by using (I) and/or (IIa) or (IIb) are governed by the sharp interface model (7.14)–(7.20) in which the same*

approximations are made. In particular, the phase field equations under assumptions (I) and (IIb), i.e.,

$$\begin{aligned} q(T) \varepsilon^2 \psi_T &= \varepsilon^2 \nabla \psi + \frac{1}{2} (\psi - \psi^3) + \frac{\varepsilon}{3\sigma(T)} [s]_{\text{eq}} \{ T - T_2 + c(T_2 - T_1) \} \\ C_v T_t + \frac{[s]_{\text{eq}}}{2} \{ T_2 + c(T_1 - T_2) \} \psi_t + \tilde{M}(\psi) c_t &= \nabla \cdot k \nabla T \\ c_t &= \nabla \cdot Dc(1-c) \nabla \tilde{G}(T, \psi, c), \end{aligned} \quad (7.52)$$

where $\tilde{M}(\psi) := [C_v T_i - \tilde{g}_i]_{1,2} - [s]_{\text{eq}} (T_2 - T_1) - \psi [s]_{\text{eq}} (T_2 - T_1)/2$ and $\tilde{G}(T, \psi, c) := [s]_{\text{eq}} (T_1 - T_2)/2 + RT \ln(c/(1-c)) + C_v T \ln T_1/T_2$, has the limit

$$\begin{aligned} C_v T_t + ([C_v T_i - \tilde{g}_i]_{1,2} - (1 \pm 1/2)[s]_{\text{eq}} (T_2 - T_1)) C_t &= \nabla \cdot k \nabla T \\ c_t &= \nabla \cdot \tilde{D} \nabla c + \nabla \cdot \frac{\tilde{D}}{T} c(1-c) \left\{ \ln \frac{c}{1-c} + \frac{C_v}{R} \ln \frac{T_1}{T_2} \right\} \nabla T \\ -k[\nabla T \cdot n]^+ &= [s]_{\text{eq}} \left\{ T_2 - (T_2 - T_1) \left(\frac{c_+ + c_-}{2} + [c]^\pm \right) v \right. \\ &\quad \left. + [C_v T_i - \tilde{g}_i]_{1,2} [c]^\pm v \right. \\ \frac{[s]_{\text{eq}}}{RT} (T_2 - T_1) &= \left[\ln \frac{c}{1-c} \right]^\pm \\ -v[c]^\pm &= [\tilde{D} \nabla c \cdot n]^\pm + \frac{\tilde{D}}{T} c(1-c) \ln \frac{c}{1-c} [\nabla T \cdot n]^\pm \\ -(q(T) v + \kappa) \sigma(T) &= [s]_{\text{eq}} (T - T_2) - RT \ln \frac{1-c_+}{1-c_-}. \end{aligned} \quad (7.53)$$

Upon making the additional approximation (III), one can eliminate the cross terms involving $c \nabla T$ etc.

The removal of this additional physics makes a major simplification in the concentration equation and leads to the traditional types of sharp interface problems [42]. Discussions of sharp interface alloy models can be found in [48, 49].

PROPOSITION 7.3. *In the limit as $\varepsilon \rightarrow 0$ with all conditions as in Proposition 7.1, except that approximations (I)–(III) are utilized, the phase field equations*

$$\begin{aligned} q(T) \varepsilon^2 \psi_t &= \varepsilon^2 \Delta \psi + \frac{1}{2} (\psi - \psi^3) + \frac{\varepsilon}{3\sigma(T)} [s]_{\text{eq}} \{ (T - T_2) + c(T_2 - T_1) \} \\ C_v T_t + \frac{[s]_{\text{eq}}}{2} \{ T_2 - c(T_2 - T_1) \} \psi_t + \tilde{M}(\psi) c_t &= \nabla \cdot k \nabla T \end{aligned}$$

$$c_t = \nabla \cdot \tilde{D} \nabla \left\{ \frac{\tilde{N}}{RT} + \ln \frac{c}{1-c} \right\}$$

$$\tilde{N} := \frac{[s]_{\text{eq}}}{2} (T_1 - T_2) \quad (7.54)$$

have an asymptotic solution which is governed to leading order by the sharp interface problem,

$$C_v T_t + \{ [C_v T_i - \bar{g}_i]_{1,2} + (1 \pm 1/2)[s]_{\text{eq}} (T_1 - T_2) \} c_t = \nabla \cdot k \nabla T$$

$$c_t = \nabla \cdot \tilde{D} \nabla c$$

$$-k[\nabla T \cdot n]_{\pm}^{\pm} = \left\{ [s]_{\text{eq}} (T_2 - (T_2 - T_1)) \left(\frac{c_+ + c_-}{2} + [c]_{\pm}^{\pm} \right) \right\} v$$

$$+ [C_v T_i - \bar{g}_i]_{1,2} [c]_{\pm}^{\pm} v \quad (7.55)$$

$$\frac{[s]_{\text{eq}}}{RT} (T_2 - T_1) = \left[\ln \frac{c}{1-c} \right]_{\pm}^{\pm}$$

$$-v[c]_{\pm}^{\pm} = [\tilde{D} \nabla c \cdot n]_{\pm}^{\pm}$$

$$- \{ q(T) v + \kappa \} \sigma(T) = [s]_{\text{eq}} (T - T_2) + RT(c_+ - c_-).$$

Note that the coefficient of c_t in the first equation can be dropped if we assume that

$$|C_v T_t| \ll |lc_t|,$$

and the first term of the third equation can be replaced by the latent heat if the difference of the latent heats of the materials is not very large. Upon neglecting the $[\dots]_{1,2}$ term in the third equation one then has the simplest heat and concentration equations. The fourth and sixth equations together determine the phase diagram. The reduction to the simplest one-phase alloy model in which c_+ and c_- are proportional (corresponding to the phase diagram of Fig. 3) follows from the fourth and sixth equations. The details are carried out in [40].

It is worth noting that the limits c_+ and c_- in each of the limiting cases is not necessarily equal to the equilibrium values c_L and c_S . The approximation which is made in the simplest models effectively substitutes the equilibrium values for the values on the two sides of interface which are in fact partly determined by dynamics.

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